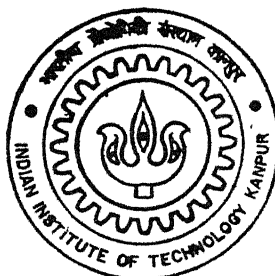# SULPHUR CONTROL OF BLAST FURNACE HOT METAL BY MANGANESE ADDITIONS.

By

Gopi Kishor Mandal

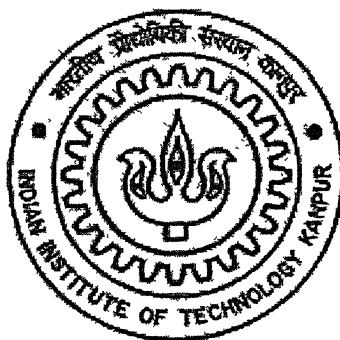DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

Indian Institute of Technology Kanpur

JUNE, 2003

SULPHUR CONTROL OF BLAST FURNACE HOT METAL BY MANGANESE ADDITIONS.

A thesis Submitted

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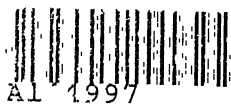for the Degree of

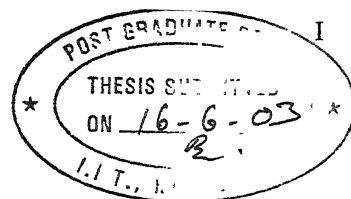**MASTER OF TECHNOLOGY**

By

Gopi Kishor Mandal

to the

DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JUNE, 2003

CERTIFICATE

It is certified that the work contained in the thesis entitled *"Sulphur Control of Blast Furnace Hot Metal by Manganese Additions"*, by Gopi Kishor Mandal has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

June, 2003

(Prof. N. K. Batra)

Professor

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Metallurgical Engg.

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(GOPI KISHOR MANDAL)

Abstract

Experiments are designed to determine the solubility of sulpher in Fe-C-Mn melts in the temperature range of 1200 to 1400ºC. Such temperatures occur during the transit of metal from the blast furnace to the mixer in a steel plant. Sulpher contents of metal decreases with an increase in Mn content of alloy at a constant temperature or with a decrease in the temperature at constant Mn level of the bath. Thermodynamic data are used to calculate the equilibrium value of sulphur as a function of temperature and manganese content. Activity of MnS is near unity in absence of any desulphuring agent. Activity of MnS would be lowered by adding certain fluxes as to produce liquid slag layer. Further experiments are designed to see the effect by maintaining slag of different composition on the sulpher content of metal at various Mn levels of the metal. A mathematical model based on mass and enthalpy balances in the lower part of the blast furnace is developed to determine the required iron ore and coke rate at different manganese level of the hot metal.

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CHAPTER I

INTRODUCTION

1.1 Importance of Sulphur Control in Steel

Sulfur may be present in the finished steel as sulfide inclusions. The volume fraction, size, shape and distribution of inclusions depend on the sulphur content, oxygen content, solidification rate, degree of hot and cold deformation and hot working temperatures. These inclusions have several effects on the processing and properties of steel as these inclusions may act as crack initiation sites and zones of weakness during deformation. In general, presence of sulfur in steel is detrimental to the ductility, toughness, formability, and weldability and corrosion resistance properties though it improves the machinability. The control of the sulphur content to low levels in the finished product is one of the oldest and broadest problems in the metallurgy of iron and steel. This control must be exercised through the action of a slag, and for this reason experimental studies of the distribution of sulpher between slag and metal were given due importance.

For general applications, sulphur content the steel, may lies in the range of 0.025 to 0.045% while for special steel, it must be below 0.01%. For high strength plate and extra quality bar products, this may mean removing sulfur to less than 0.005%. Free cutting steel is the only grade of steel where the sulphur content is deliberately kept high viz. 0.22wt% or more. Thus, it is essential that strict control of sulphur in steel be maintained.

1.2 <u>Origin of Sulphur in Steel</u>

The major source of sulphur in steel is the presence of sulphur in the hot metal produced by the blast furnace. Sulphur enters in iron blast furnace via coke and it gets distributed between the slag and metal phases in the lower part of the furnace. Less then 10% of sulphur leaves with the flue gases. In the blast furnace, as the coke burns at the tuyeres, sulphur is picked up by the H_2 and CO gases to form H_2S and COS . As these gases come in contact with iron bearing and CaO bearing materials, sulpher is absorbed to form FeS and CaS and it descends back to the lower part along with the rest of the materials in the molten form. Further transfer of sulphur from metal to the slag or vice versa occurs in the hearth.

The main control of sulphur is done in the blast furnace stage itself as the extend of sulphur removal during steel making is small. It is estimated that 80-90% of the sulphur input is removed in the slag in the blast furnace while the rest goes in the metal. The factors that control the sulphur content in blast furnace include the coke rate, sulphur content of coke, slag volume and the sulphur distribution ratio alpha (α) i.e.(%S in slag)/[%S in hot metal]. Mathematically sulphur balance gives the following:

$$[\%S]_{HM} = ((\%S)coke * W_{coke}) / (1000+ \alpha * W_{SL})$$

Where $W_S = (\%S)coke * W_{coke}$

=Sulpher in charge per 1000 Kg of metal, and

W_{SL}= Slag rate (Kg per 1000Kg of metal).

Since slag rate is kept low for other advantages and coke rate and coke quality cannot be changed appreciably, low sulphur can be achieved only at high sulphur distribution ratios.

Sulphur distribution between slag and metal may be described as follows:

$$[FeS] + (CaO) = (CaS) + (FeO)$$
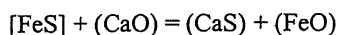
Factors that control the sulphur distribution rate are summarized below:

(1) High basicity of the slag.

(2) High lime content of the slag.

(3) Low FeO content of the slag.

(4) High temperature.

(5) A fluid slag.

(6) Stirring in the bath.

(7) Presence of elements such as carbon, silicon, phosphorus in metal as they increase the activity coefficient of sulphur in the liquid metal.

Under slag commonly occurring in the basic oxygen steel making, the sulphur distribution ratio i.e.(%S)/[%S] may lies in the range of 5 to 10. Under blast-furnace conditions, however, desulphurization ratios of 50 to 100 are readily obtained as FeO content of the slag is very low.

1.3 <u>External Desulphurization</u>

Techno- economic considerations may not justify sulphur removal to low levels either in blast furnace or in LD steel making. External desulphurization of hot metal has therefore, great importance. Desulphurizing agents such as soda ash, lime, calcium carbide or magnesium are either added or injected to the metal in a suitable manner to enhance the rate of sulphur removal from the metal to the slag. Various methods have been used for external desulphurization during the last two decades and the same have been summarized by many investigators. Due and effective removal of sulphur rich slag will be important as, otherwise, sulphur reversion could occur during oxygen steel making.

1.4 Scope of the Present Work

Many studies have been done in the last few decades to control the sulpher content in steel for its improved mechanical properties. In the present work experiment are designed to determine the solubility of sulpher in the carbon saturated iron with or with out addition of manganese to the melt in the temperature range of 1200 to 1400°C. Such temperatures occur during the transit of metal from the blast furnace to the mixer in a steel plant. Thermodynamic data are used to calculate the equilibrium value of sulphur as a function of temperature and manganese content. Further experiments are designed to see the effect by maintaining slag of different composition on the sulpher content of metal at various manganese levels of the metal. Effect of increasing manganese content in blast furnace metal by adding manganese ore on the coke rate has been studied by using a mathematical model based on enthalpy and materials balances in the lower part of the furnace.

CHAPTER II

LITERATURE SURVEY

In this chapter, attempts are made to review briefly the work carried out by different investigators.

2.1 Activity of sulphur in liquid iron alloys

Chipman and co-workers[4] equilibrated the melt of iron carbon alloys with gases containing hydrogen and hydrogen sulphide. Gas metal reaction would be described as follows:

$$[S] + H_2 (g) = H_2S (g) \tag{2.1}$$

$$K = P_{H2S} / (P_{H2} * a_S) \tag{2.2}$$

Where P_{H2S} and P_{H2} are the partial pressure of H_2S and H_2 respectively in the gas mixture and a_S is the activity of sulphur in the liquid metal which is related to its concentration in the metal i.e.

$$a_S = f_S * [wt\%S] \tag{2.3}$$

Where f_S is the activity co-efficient of sulpher in the liquid metal and [wt%S] is the percentage of sulpher in the melt.

In a multicomponent system containing N solutes, f_S given by the following equation:

$$\log f_S = \sum_{j=1}^{N} e_S^j . [wt\%j] \tag{2.4}$$

Where e^j_s is henrian activity interaction parameter for 1wt% standard state and is defined below:

$$e^j_s = (\ \partial \log f_S / \partial wt\%j)_{wt\%Fe \to 100} \tag{2.5}$$

As concentration of all solute tends to zero, f_S must tend to one. For very dilute solution, equation (2.2) may be rewritten as follows:

$$K = P_{H2S}/(P_{H2}*f_S*[wt\%S]) = K'/f_S \tag{2.6}$$

$$\text{Where } K' = P_{H2S}/(P_{H2}*[wt\%S]) \tag{2.7}$$

At any concentration of sulphur, K' can be found by fixing P_{H2S}/P_{H2} ratios and finding the corresponding [wt%S] in the melt. Plots of experimentally determined log K' by Shearman et al[18] at 1600°C and 1615°C versus sulpher percent are shown in *Fig. 2.1*. The experimental data of Morris and Willams[19] and Morris and Buehl[3] are also shown in the figure. The equilibrium constant K is determined from the intercept of the line at zero concentration and for any finite concentration activity co-efficient of sulphur is determined by using equation (2.6) i.e. taking rate of K' to K.

2.1.1 Fe-S System

Standard free energy of formation of H_2S from gases such as H_2 and S_2 has been reported by Banny and Chipman [2] as follows:
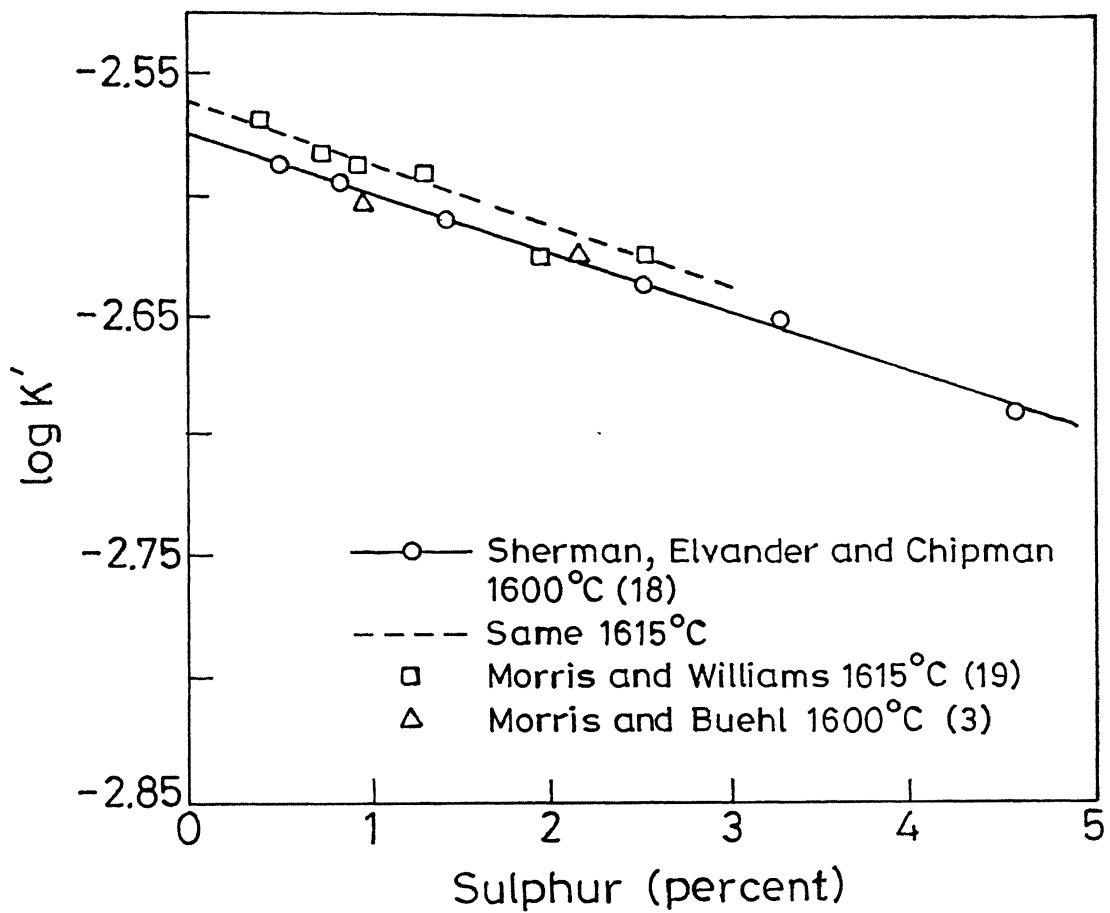
Fig. 2.1 Computed values of constant K′ by different investigators. (Ref. 3, 18 and 19)

$$H_2 \text{ (g)} + 1/2 S_2 = H_2 S \qquad (2.8)$$

$$\Delta G^* = -21820 + 11.92T \text{ cal} \qquad (2.9)$$

They studied gas metal equilibrium and obtained the data below:

$$[S]_{wt\%} + H_2 \text{ (g)} = H_2 S \text{ (g)} \qquad (2.10)$$

$$\Delta G^0 = 10750 + 6.13T \text{ cal} \qquad (2.11)$$

Combining (2.8) and (2.10) one may get

$$1/2 S_2 = [S]_{wt\%} \qquad (2.12)$$

$$\Delta G^0 = -32280 + 5.6T \text{ cal} \qquad (2.13)$$

Activity co-efficient of sulphur fs was reported to vary with sulphur content of iron at 1600^0C as follows:

$$\log f_S = -0.0282*[\%S] \qquad (2.14)$$

This gives value of interaction parameter as below:

$$e^s_s = -0.0282 \qquad (2.15)$$

2.1.2 Ternary Systems

2.1.2.a Iron – Carbon – Sulphur System

Morris and Buehl [3] determined the effect of carbon on the activity coefficient of sulpher in the metal phase. Results are plotted in *Fig 2.2*. A molten iron-carbon alloy was brought to equilibrium at constant temperature with a mixture of H_2 and H_2S of constant composition by bubbling the gas through metal. Results showed that carbon had a decided influence on the activity coefficient of sulphur. Activity coefficient of sulphur increased with a rise in temperature. However, the temperature effect was small except at carbon saturation, where a rise in temperature is accompanied by an increase in the carbon content of the metal and by a rise in sulphur activity coefficient resulting from the carbon increase.

Values of henrian activity interaction parameter is around 0.12 upto carbon concentrations of 1-2 wt%, but the carbon pct. beyond 2%, log f_s versus [%C] plot is not linear and equation (2.4) cannot be applied directly to find e^c_s values.

Morris and Buehl [3] used 4.35% carbon in iron as its standard state to solve the problem and reported the following:

$$1/2S_2 (g) = [S]_{(4.35\%C)} \qquad (2.16)$$

$$\Delta G^0 = -23880 + 3.9T \text{ cal} \qquad (2.17)$$
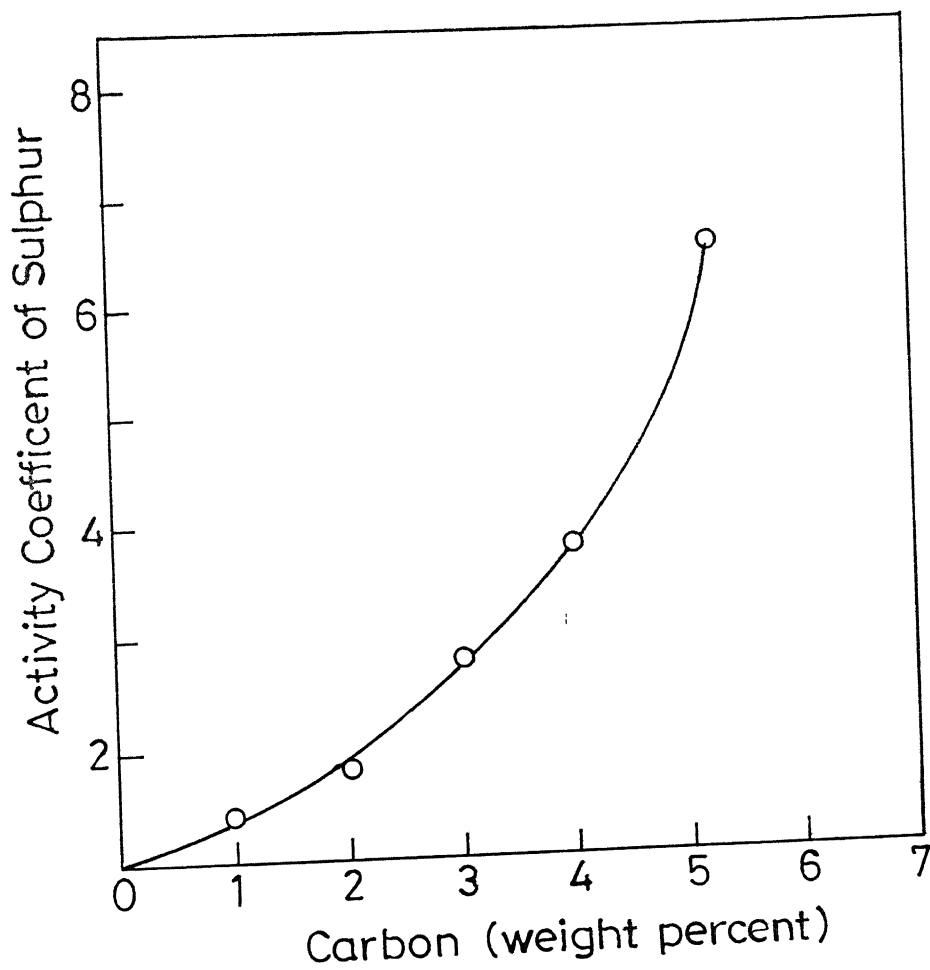
Fig. 2.2 Effect of carbon content on activity coefficient of sulphur in iron at 1600°C. (Ref. 3)

f^c_s is found to be 4.2 at 1600^0C and 4.35% carbon. At carbon content of melt near saturated values activity coefficient of sulphur in the melt was determined as follows:

$$\log f^c_S = \log 4.2 + 0.24(X\text{-}4.35) \qquad (2.18)$$

where X= wt% of carbon in the melt.

2.1.3 <u>Effect of Alloying Elements on Activity of Sulphur</u>

Sherman and Chipman[4] studied various ternary systems in relation to the activity of sulphur. Results of experiments are shown in *Fig 2.3*. Calculated values of interaction parameter are included in *Table 2.1*.

Pattjoshi[1] proposed a regular solution model for finding the activity coefficient of sulphur at any temperature lower than 1600^0C as data existed in the literature only at 1600^0C. He determined the activity coefficients of sulphur and manganese with reference to the infinite dilute solution state on 1 wt% standard state scale as follows:

$$\log f_S = e^C_S \, [\text{wt\% C}] + e^{Mn}_S \, [\text{wt\% Mn}] + e^S_S \, [\text{wt\% S}] \qquad (2.19)$$

$$\log f_{Mn} = e^C_{Mn} \, [\text{wt\% C}] + e^{Mn}_{Mn} \, [\text{wt\% Mn}] + e^S_{Mn} \, [\text{wt\% S}] \qquad (2.20)$$

Carbon saturation value in the melt was calculated as follows[22]:

$$[\text{wt\% C}]_{SAT} = 1.34 + 0.00254 \, t \, (^0C) - 0.4 \, [\text{wt\% S}] + 0.04 \, [\text{wt\% Mn}] \qquad (2.21)$$
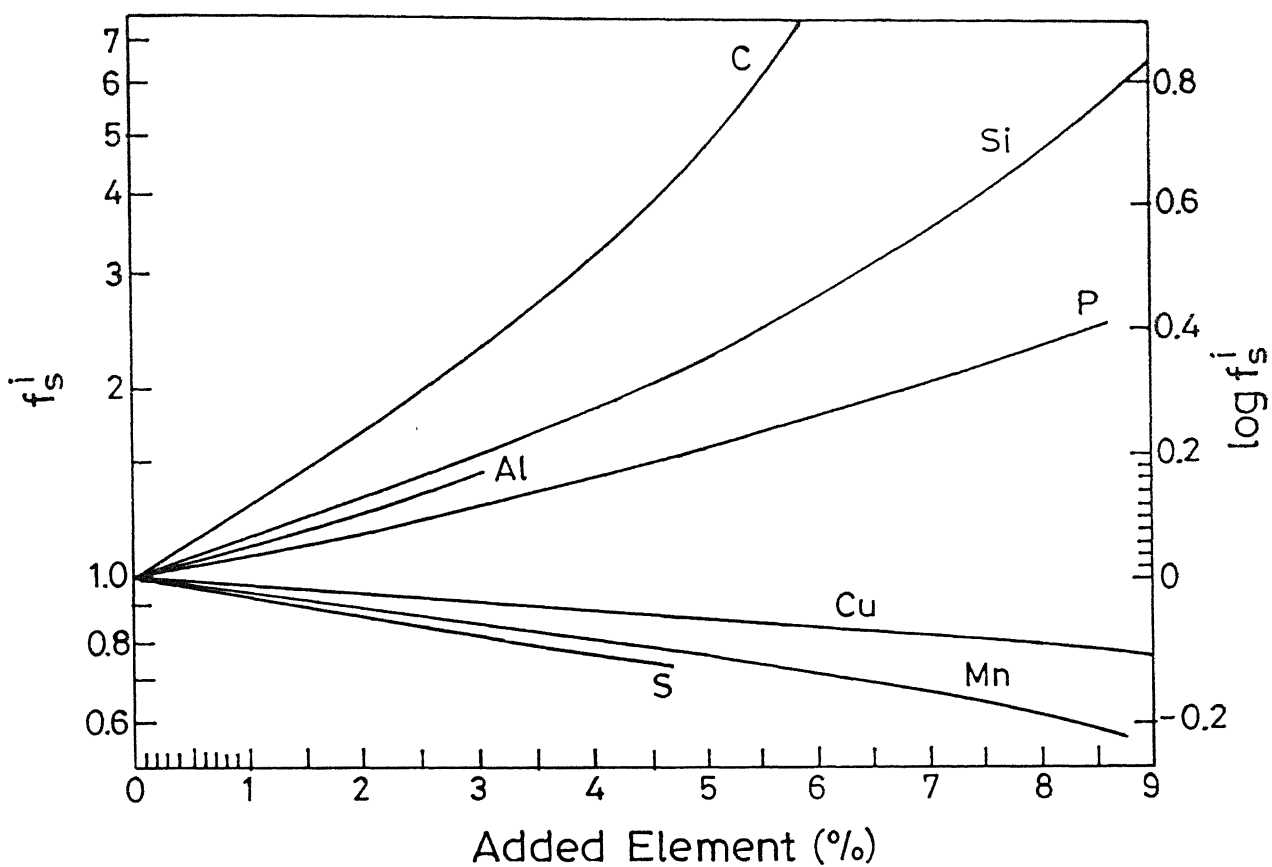
Fig. 2.3 Effect of alloying element on activity coefficient of sulphur in iron at 1600°C. (Ref. 4)

i=third component	e^i_s
S	-0.028
C	+0.113
Si	+0.065
P	+0.043
Al	+0.054
Cu	-0.013
Mn	-0.025

Table-2.1[4] : **Effects of small concentrations of added substance on activity co-efficient of sulphur.**

2.2 Sulpher Distribution Between Metal and Slag in Blast Furnace

In the blast furnace, the sulphur reaction may be represented by the following:

$$CaO + [S] + [C] = CaS + CO \qquad (2.22)$$
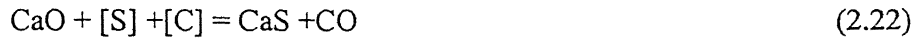
The temperature dependence of equilibrium constant, K_S is given as

$$\log K_S = -6010/T + 5.935 \qquad (2.23)$$

$$K_S = (a_{CaS} * P_{CO})/(aCaO * [\%S] * f_S * a_C) \qquad (2.24)$$

The activity of CaS and CaO relative to pure solids may be represented in term of weight percent of CaS and CaO as shown below

$$a_{CaS}/a_{CaO} = (56 * (\%S) * \gamma_{CaS})/(32 * (\%CaO) * V_{CaO}) \qquad (2.25)$$

It is assumed the sulphur is present in the slag as CaS. In the graphite saturated melt, the activity co-efficient of sulphur, f_S is around 7. Sulphur distribution rate may be written as follows.

$$\alpha = (\%S) / [\%S] = 4 * \gamma_{CaO} * (\%CaO) * K_S / P_{co} * \gamma_{CaS} \qquad (2.26)$$

Turdogan[11] as well as Biswas[12] has shown that the primary reaction for the transfer of sulphur from metal to slag must not be reaching equilibrium in blast furnace due to three phases involved in this reaction. Similarly the authors concluded that manganese and silicon content of metal could not be predicted by the slag metal reaction equilibria in the hearth or bosh region in the furnace. However, coupled reactions more or less reached equilibrium in the blast furnace.

One coupled reaction involving manganese and sulphur is given below:

$$CaO + [Mn]_{wt\%} + [S]_{wt\%} = CaS + MnO \qquad (2.27)$$

$$\log K_{MnS} = 9080/T - 5.832 \qquad (2.28)$$

$$K_{MnS} = K_S/K_{Mn} = (a_{CaS}*a_{MnS})/(a_{CaO}*[\%S]*[\%Mn]*f_S*f_{Mn}) \qquad (2.29)$$

The graph between (%S)/[%S] vs. [%Mn]*(CaO)/(%MnO) is given in *Fig. (2.4)*. With the given data, sulphur – manganese equilibrium at graphite saturation is represented as

$$\text{Log} (((\%S)*(\%MnO))/([\%S]*[\%Mn])) = 9080/T - 5.832 + \log(\%CaO) \qquad (2.30)$$
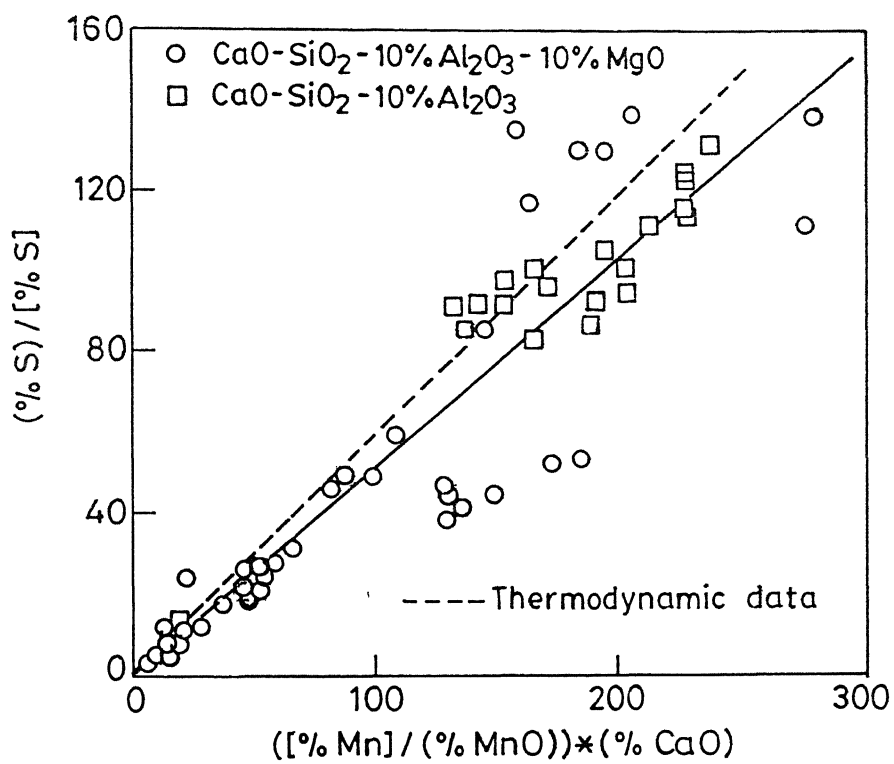
Fig. 2.4 Sulphur - manganese reaction equilibrium at graphite saturation at 1500°C.

Coupled reaction that involve silicon and sulphur is:

$$CaO + 0.5 [Si] + [S] = CaS + 0.5 SiO_2 \qquad (2.31)$$

$$\log K_{SiS} = 9080/T - 5.832 + 1.396 * B \qquad (2.32)$$

$$\alpha = (\%S) / [\%S] = (154 * K_{SiS} * \gamma_{CaO} * (\% CaO) * [\%Si]^{0.5}) / (\gamma_{CaS} * \gamma_{SiO2} * (\%SiO_2)) \qquad (2.33)$$

$$\log (((\%S)*(\%SiO_2)^{0.5})/([\%S]*[\%Si]^{0.5})) = 9080/T - 5.832 + \log(\%CaO) + 1.396B \qquad (2.34)$$

2.3 External Desulphurisation of hot metal

The methods used for desulphurization of melt outside the blast furnace and before the steel making fall broadly into the following categories:

1. Use of soda ash (Na_2CO_3) or caustic soda (NaOH);

2. Use of lime (CaO),

3. Use of calcium carbide (CaC_2) and calcium cyanamide (CaNCN) with or with out soda,

4. Use of magnesium or magnesium coke.

Soda ash is usually employed for ladle desulphurization. Sodium possesses great affinity for sulphur and forms sodium sulphide according to:

$$[FeS] + Na_2CO_3 \text{ (or NaOH)} = Na_2S + FeO + CO_2 \text{ (or } H_2O) \qquad (2.35)$$
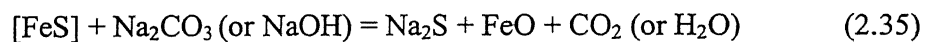
Na_2O is obtained in liquid state above 900^0C, a temperature much below that of hot

metal. Writing Na_2O instead of carbonate or hydroxide,

$$[FeS] + Na_2O + [C] = Na_2S + [Fe] + CO \qquad (2.36)$$
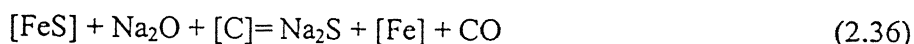
Presence of silicon gives the following reaction:

$$2[FeS] + 2Na_2O + [Si] = 2Na_2S + 2[Fe] + SiO_2 \qquad (2.37)$$
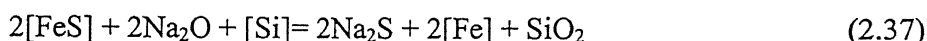
Silica formed in the above reaction may combined with Na_2O thereby reducing its activity, this will cause for the removal of sulphur from the metal difficult.

Due to importance of external desulphurization of hot metal, many studies on the kinetics of desulphurization by injection of calcium carbide, magnesium, lime and calcium alloys etc in the blast furnace iron have been reported in the literature. Most of the studies are done on pilot plant scale. The various methods of pretreatment of metal are summarized in *Table 2.2*.

(2.3.1) Kinetics of External Desulphurisation

Lime is capable of reducing sulphur content of cast iron and blast furnace iron to very low level but the rate of desulphurisation is low. It may be attributed to solid reaction products that could form diffusion barrier on the surface of lime particles. Craig F. Landefeld[14] have studied effect of lime and spar addition in the melt. Results are

Desulphurizing agent	Mode of addition	Reagent quantity (kg/THM)	Sulphur range
Soda ash	Bulk addition	10	0.1 to 0.03
Lime	Injection	10- 20	0.05 to 0.02
Lime & soda ash mixture	Injection	8 –10	0.05 to 0.02
Calcium carbide	Injection	4	0.05 to 0.02
Magnesium Coke	Plunging	0.7	0.048 to 0.022
Magnesiumm granules	Plunging	0.7-1.2	0.05 to 0.005

Table 2.2: **Method of Desulphurization**

plotted in *Fig 2.5.*Addition of spar increases the rate of desulphurization. However, under the experimental conditions, the rate of desulphurization was found to remain unchanged beyond 8% spar. This is attributed to saturation of liquid phase with $3CaO.SiO_2$ phase. They also compared the effect of silicon and manganese on desulphurization rate. Results are plotted in *Fig 2.6.*

Injection of magnesium into blast furnace iron has been a major problem. Boiling point of magnesium is 1107^0C and it tends to explode when plunged into hot metal whose temperature commonly exceeds 1200^0C. Iron et al. [15] have circumvented the problem by vapourizing the magnesium before it was injected into iron and studied the kinetics of desulphurization, based on MgS particles.

External desulphurization of hot metal by calcium carbide injection in the melt is a well established process. Chang[16] have studied the kinetics of desulphurization of hot metal at temperature of 1350^0C and reported that the oxygen activity of the bath is very important factor during desulphurization. Control of hot metal oxygen activity to low levels improves the efficiency of desulphurization process. They found that there was an incubation period during which reagent created an appropriate slag layer before it began to remove the sulphur. With no slag, the melt surface is susceptible to oxidation and a liquid layer of iron oxide is probably formed. This slag could then oxidize the calcium sulphide produced during the desulphurization process, thus, reverting the sulphur into iron melt. The net effect was that no desulphurization occurred in the incubation period. As the partially oxidized CaC_2/CaS particles continue to build up on the surface during injection, conditions would be come more and more reducing, there by favoring desulphurization. In case of unreactive slag mixture of $CaO-SiO_2$, an oxide reach slag could be formed, which must be reduced before effective desulphurization could proceed.
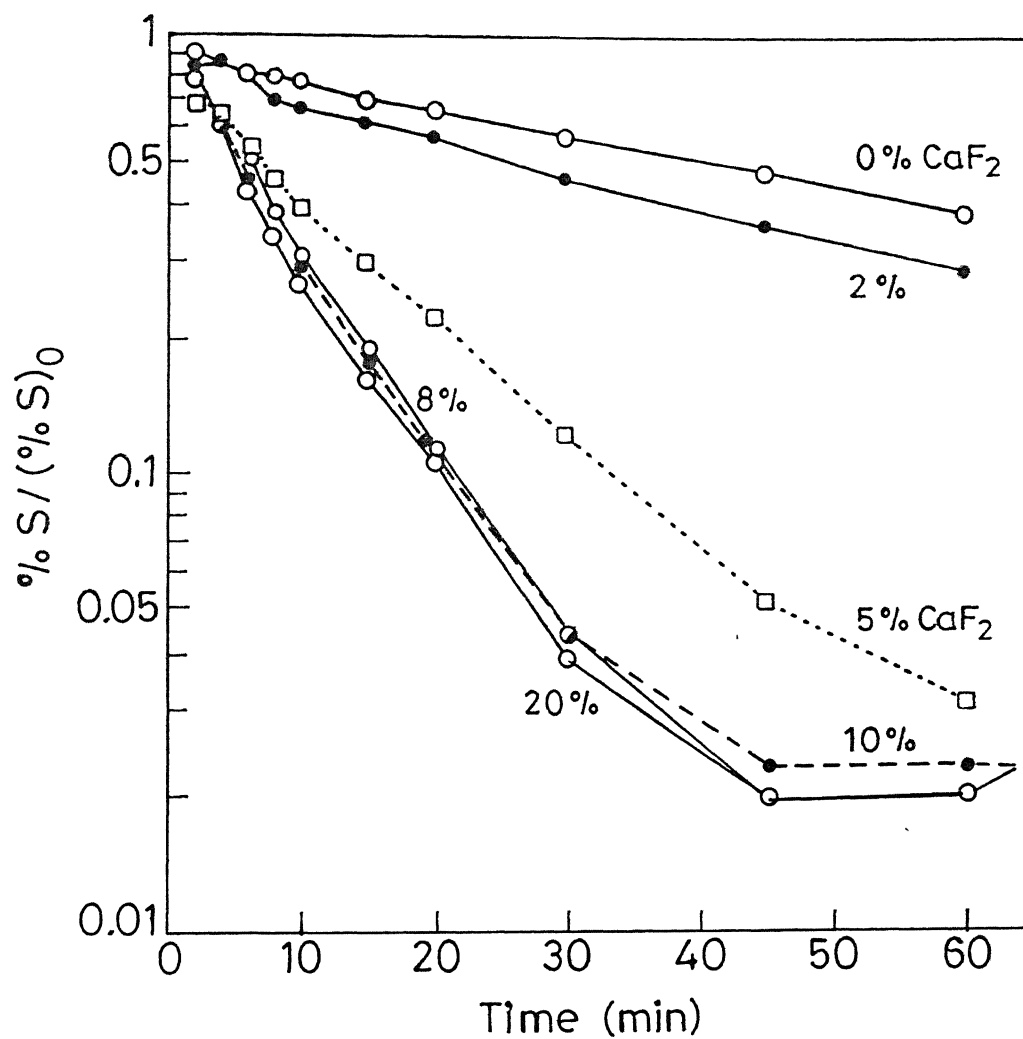
Fig. 2.5 Effect of CaF_2 percentage on desulphurization.
(Ref. 14)
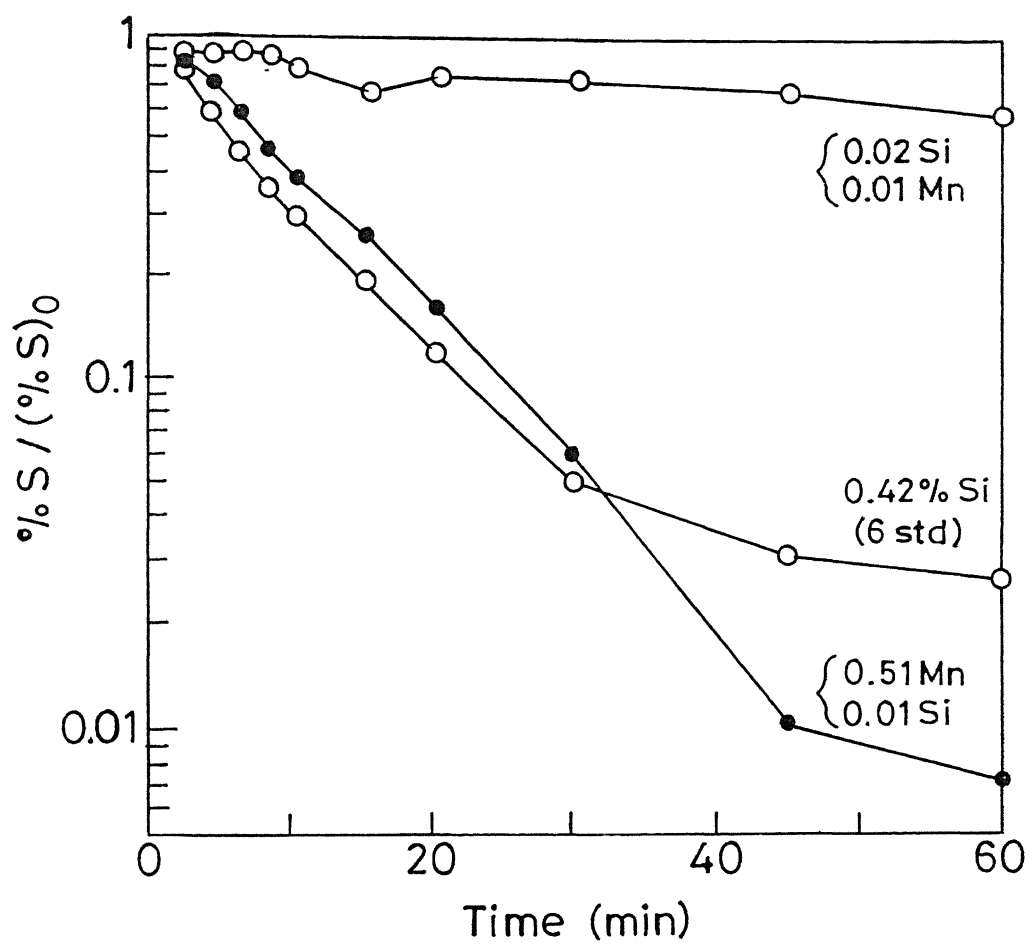
Fig. 2.6 Comparison of the effects of Si and Mn
(Ref. 14)

Tabala[17] proposed a reaction mechanism according to which calcium carbide first decomposed to form graphite and calcium vapours. The calcium vapours then reacted with sulphur to form a layer of calcium sulphide over the graphite layer. The layers of graphite and calcium sulphide progressively thicken so that calcium vapor must diffuse through them. Chiang et al.[18] showed that the rate of calcium diffusion through the product layer was 50 times greater than the rate of sulphur diffusion through the particle/liquid boundary layer. Based on this fact, they concluded that desulphurization rate was determined by the rate at which sulphur diffused through the liquid boundary layer around the particles rather than the product layer.

Freezing of top layer of metal in the ladle may occur in many desulphurization processes to give high scull losses. This makes addition of desulphurizing agent to bath very difficult.

A study of the kinetics of sulphur transfer across a slag metal interface under reducing conditions by Chang Lo-Ching and Goldman[20] shows the followings:

(1) The net rate of transfer of sulphur from metal to slag increases very rapidly with increasing basicity of slag. The net rate of sulphur transfer is influenced by changes of slag composition.

(2) The activity coefficient of sulphur in molten iron is increased by the presence of carbon. Thus for a given slag at a given temperature the higher the concentration of carbon, the better will be the desulphurization of the metal.

The rate curves for five slags composition at 1540^0C are shown in *Fig-2.7*.
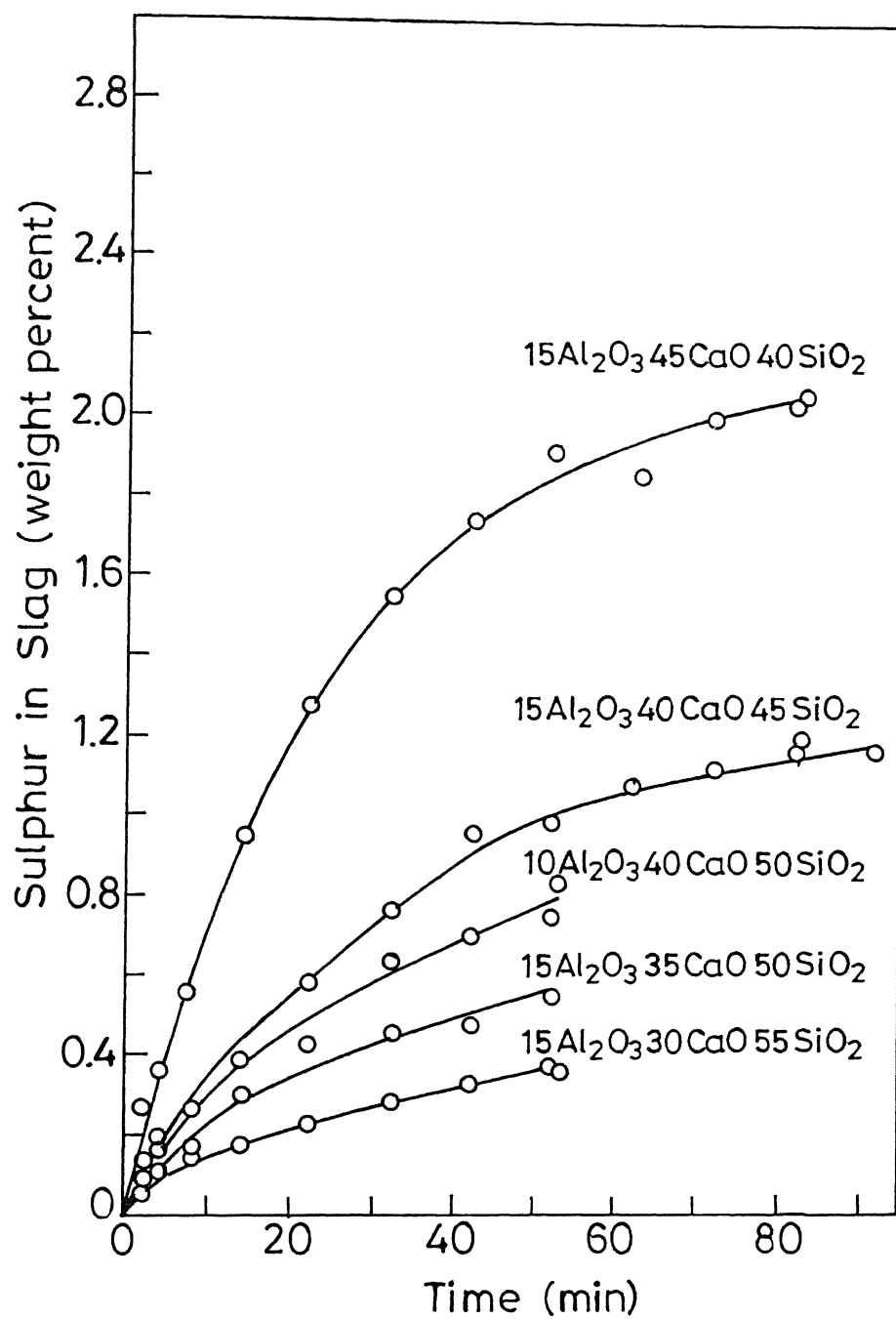
Fig. 2.7 Rate curves. (Ref. 20)

2.4 Effect of Manganese on Desulphurisation

Oelsen[13] studied the solubility of MnS in carbon saturated blast furnace iron and reported that the solubility of MnS in the melt decreased with decreasing temperature. Results are plotted in *Fig2.8.* Si and P content of the blast furnace iron was not specified by Oeslen.

Morís[6] studied the effect of manganese on sulphur content of graphite saturated iron alloy by step wise addition of manganese as well as stepwise cooling of a melt containing both manganese and sulphur. Results are plotted in *Fig 2.9.* They concluded that manganese alone could not be an efficient desulphurizer except at temperatures below the normal operating range. However, in the presence of an oxide slag, manganese may be more effective as a desulphurizer than is indicated in *Fig 2.9* due to lowered activity of manganese sulphide in the slag.

Grant[10] studied the effect of Mn and MnO on sulphur content of metal when added to initial charge or during the course of a heat. Addition of MnO led to an immediate and temporary reversion of sulphur to the melt because of increase in oxygen potential of slag. Effect of manganese on desulphurization rate was very small and it was confined to slag of lower basicity.

Pattjoshi(1) argued that with an increase in manganese level in the melt, there could be increase in transfer of sulphur to slag phase due to the following:
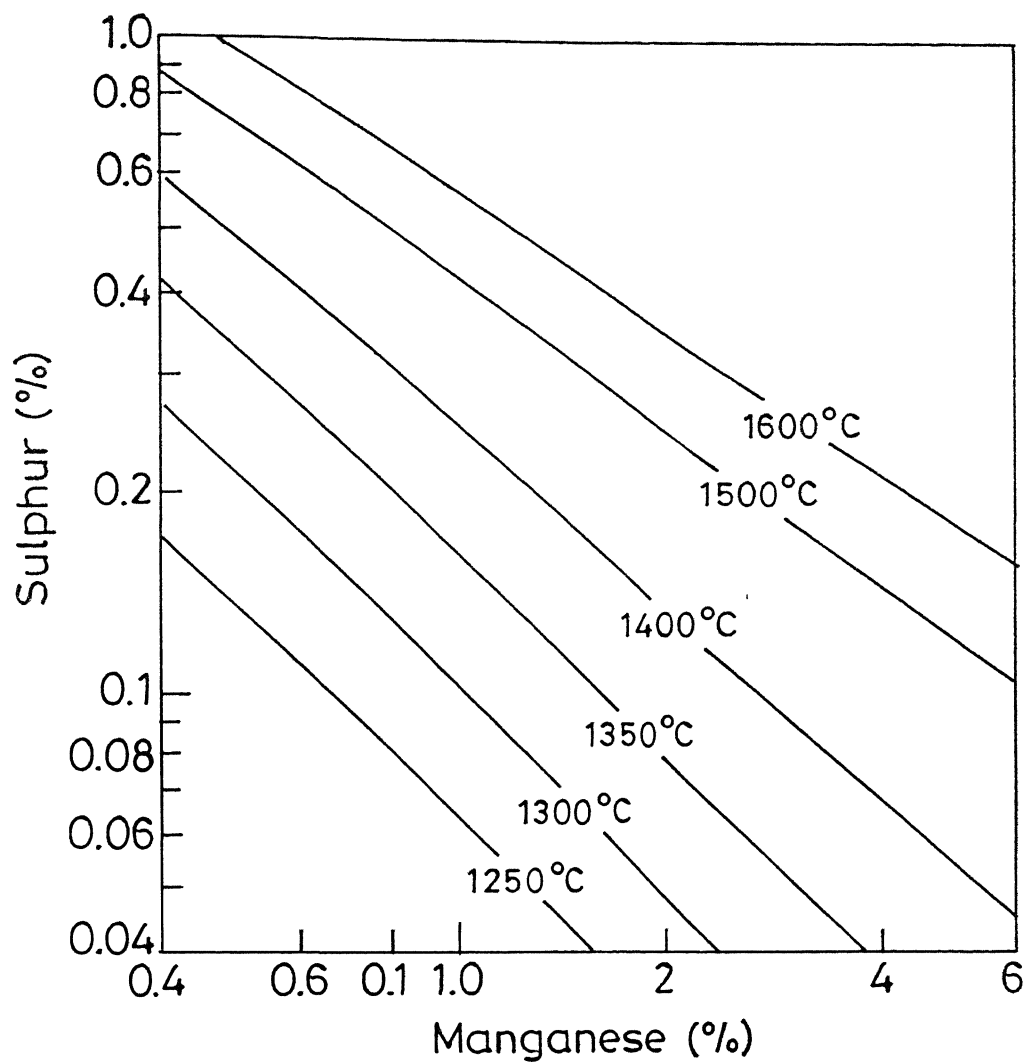
Fig. 2.8 Manganese sulphide solubility in the iron-carbon melt. (Ref. 13)
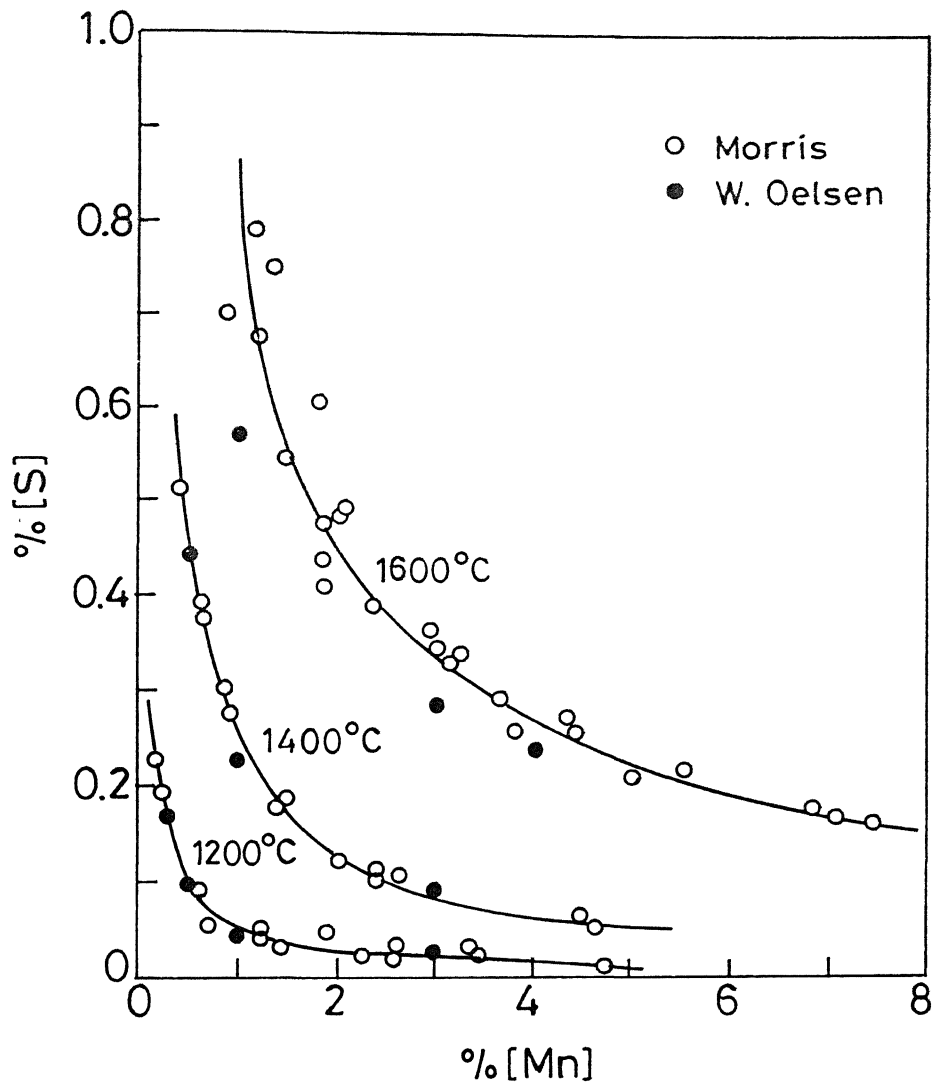
Fig. 2.9 Effect of manganese on the sulphur
content of the carbon saturated melts
of iron in equilibrium. (Ref. 6)

1 The activity of MnS in the slag is lowered due to the presence of liquid lime based slag. They would reduce the sulphur content of the metal at equilibrium with the slag phase.

2. Presence of manganese enhanced the rate of sulphur removal by CaO in the slag as per the following coupled reactions:

$$(CaO) \ + \ [S] = (CaS) + [O]$$
$$[O] \quad + \ [Mn] = (MnO)$$
$$(CaO) + [S] + [Mn] = (CaS) + (MnO)$$
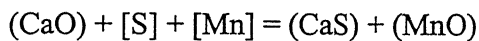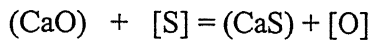
3. Mn in the melt reacts with SiO_2 in the slag to give silicon in the melt.

$$2[Mn] \ + SiO_2 \ = 2 \ (MnO) + [Si]$$
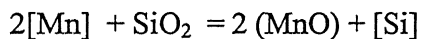
This could increase the basicity of the slag as well as activity coefficient of sulphur in the melt leading to lower sulphur level in the metal. He suggested that all three factors might be responsible for lowering the S level in the melt.

CHAPTER III

EXPERIMENT

3.1 Equipments

3.1.1 Silicon Carbide Furnace

A silicon carbide furnace having outer diameter 600 mm and 400 mm high was used for the study. Schematic diagram of the furnace is shown in *Fig 3.1*. The furnace tube consisted of one end closed alumina tube having 50 mm internal diameter and 450 mm long. It rested on a refractory base at the bottom. The tube was filled with alumina powder at bottom upto the level of high temperature zone in the furnace. The power of the furnace was supplied using a 40 amp single phase oil cooled auto-transformer with 220 volts input and 0-240 volts output. One on – off temperature controller and magnetic relay switch were used to keep the temperature of the furnace in a narrow range. Platinum – Platinum + 10% Rhodium thermocouple was used to measure the temperature.

3.1.2 Super Kanthal Raising Hearth Type Furnace

One raising hearth type furnace i.e. model 70 R 10 manufactured and installed by Bysakh and Company, Calcutta was used for the preparation of master slag in the present study. It has got dimensions of 200 mm square $\times$ 300 mm high. The furnace consists of 3 numbers of U shape Molybedum Disilicide heating elements of type '33'. The furnace has got Pt – 6% Rd/Pt – 30% Rd thermocouple for temperature measurements and a proportional temperature controller. The furnace required a power supply of 2 phase AC of 400 volt. The furnace bottom has an opening of 120

mm and its refractory end was raised or lowered using a lever arm for closing and opening the furnace bottom respectively.

3.1.3 Digital Balance

A digital balance supplied by the Mettler, Germany, was used to determine the weight upto the accuracy of 0.1 mg for doing chemical analysis of the samples for sulphur determination.

3.1.4 Sulphur Analysis Set – up

For analyzing sulpher in the samples, the set up consisted of the following equipments.

1. 250 CC conical flask,

2. 250 CC separating funnel,

3. B/34 glass joint,

4. Glass tubes (6mm internal dia.),

5. 100 cc measuring cylinder, and

6. 1500 watts hot plate.

Titration set up consisted of a 50 cc burette and a 10cc pipette. The set up is shown in *Fig 3.2.*

3.1.5 Platinum Crucible and Lid

One platinum crucible of weight 19.74 gm and a platinum lid of weight 8.2 gm were used to carry out the melting of slag.

3.1.6 Photospectro meter

Manganese analysis was done using Ultra – Violet – Visible Range Spectro-photometer supplied by Systronics, New Delhi.

3.1.7 Strohlein Apparatus

Carbon analysis was done using Strohlein apparatus. The Strohlein apparatus is shown in *Fig-3.3.*
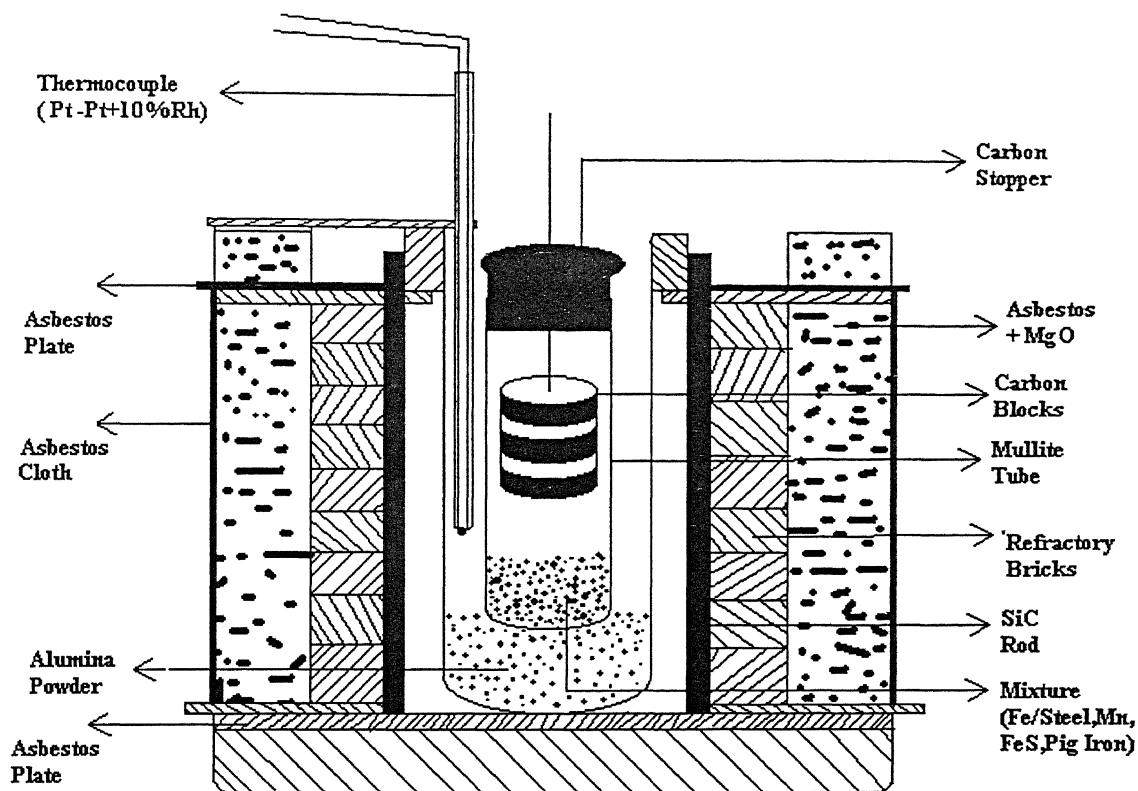
Fig 3.1: SCHEMATIC DIAGRAM OF SILICON CARBIDE FURNACE
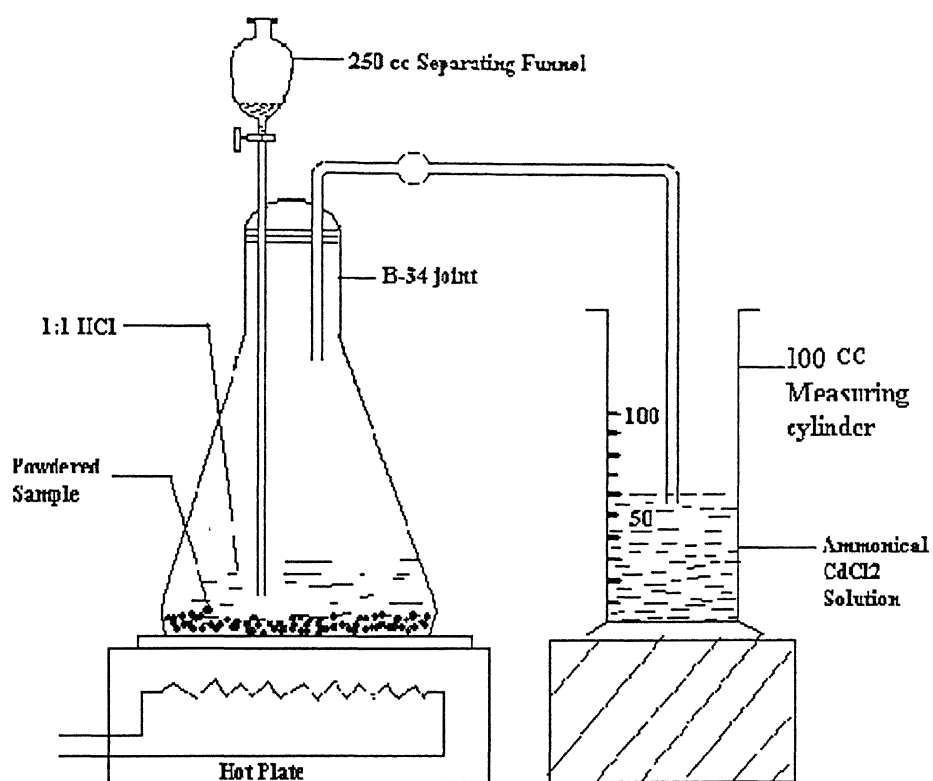
Fig 3.2: SCHEMATIC SET UP FOR SULPHUR ANALYSIS

3.2 Materials

3.2.1 Materials for Melting

Solid pig iron samples obtained from Rourkela Steel Plant were suitably broken into small pieces. The pieces were washed with acetone before being used for the experiments. Manganese used was 99.9% pure in the powder form and obtained from USA. FeS used was of local made. Carbon used in the form of graphite powder. Lime was obtained by calcination of pure calcite in the laboratory at 1000^0C for one hour. Iron ore used to get metallic iron by aluminothermic reduction was obtained from TISCO, Jamshedpur, India and finely divided aluminium powder used was obtained from Central Drug House (P) Ltd, New Delhi, India.

3.2.2 Mullite Tube

The mullite tube was of 2.5 cm internal diameter and 300 mm length obtained from Kumar Refractory and Co.

3.2.3 Graphite Rods

The graphite rod was of 4 cm diameter was machined in the laboratory to make graphite crucible of 3.5 cm internal diameter, 3.8 cm of outer diameter and 6.5 cm length.

3.2.4 Sampling tube

4 mm diameter and 1m long quartz tubes were used for drawing metal samples using an aspirator. One tube could be used for drawing 5 – 6 samples.

3.2.5 Chemical Reagents

Standard chemical reagents used in the study are listed below:

1. Hydrochloric Acid (HCl)

2. Sulphuric Acid (H_2SO_4)

3. Ammonical Cadmium Chloride ($CdCl_2$) Solution

4. Potassium iodide

5. Sodium thiosulphate

6. Potassium Dichromate ($K_2Cr_2O_7$)

7. Sodium Carbonate Anhydrous (Na_2CO_3)

8. Sodium thiosulphate ($Na_2S_2O_3$)

9. Starch

10. Lime used was obtained from Ranbaxy India Limited, New Delhi.

11. Quartz fine granular supplied by E. MERCK AG. DARMSSTADT, Germany

12. Alumina

3.3 Experimental Procedure

3.3.1 Master Slag Preparation

The slags of following compositions were prepared in the laboratory. The constituents of the slag i.e. lime, silica, and alumina were charged to a platinum crucible which was heated in a raising hearth type furnace at 1500^0C for about 30

minutes. The molten slag was poured into a platinum lid of 2.5 cm diameter and the slag was recovered by breaking the solidified mass after cooling.

The compositions for the preparation of different slag's are given in *table 3.1*.

Sl. No.	CaO (gm)	SiO$_2$ (gm)	Al$_2$O$_3$ (gm)	Basicity
1	36	44	20	0.8
2	40	40	20	1.0
3	44	36	20	1.2

3.3.2 Preparation of Metallic Iron

The main raw materials required for the preparation of metallic iron include the iron ore (Fe$_2$O$_3$), finely divided aluminium powder, steel turnings, carbon, limestone, sand, and potassium permanganate (KMnO$_4$). A fuse of magnesium ribbon was required to initiate the reaction. The experiment was carried out in a magnesite lined steel reaction vessel which was conical in shape and kept in open area. Mixture was transferred to the preheated reaction vessel and fired the charge by means of a fuse of magnesium ribbon. The reaction was completed within couple of minutes and alumina slag was floated on top. Iron was obtained by aluminothermic reduction of iron oxide by the following reaction:

$$2/3\ Fe_2O_3 + 4/3\ Al = 4/3\ Fe + 2/3\ Al_2O_3; \Delta H = -136500\ cal/gm\ mole \qquad (3.1)$$
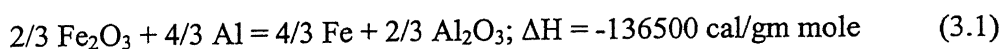
Efforts to make the metal in a mullite tube by preheating the mixture resulted in an explosion that caused damage in the workplace and the furnace involved in the operation. Thus, it was considered a safety hazard.

3.3.3 Melting of Metal and Slag in Silicon Carbide Furnace

3.3.3.1 Determination of Solubility of Sulphur in Iron – Carbon – Manganese Melts.

In one category of experiments the blast furnace metal pieces along with required additives such as iron/steel, iron sulphide, manganese powder and carbon were taken in a mullite tube. The mullite tube was lowered into the hot zone of the silicon carbide furnace when temperature was around 1250^0C. The carbon blocks were placed inside the tube with the help of molybdenum wire as shown in *Fig – 3.1* to make the environment reducing in nature. A carbon stopper was used at the top of the mullite tube. The furnace was maintained at the required temperature of around 1400^0C for 30 minutes before samples were drawn in a quartz tube using an aspirator. Carbon blocks and carbon stopper were maintained through out the duration of the experiment except for a few minutes when stirring was done using a carbon rod of 6mm diameter or when samples were drawn. After drawing the sample furnace was cooled to around 1325^0C and held there for 30 minutes before drawing the sample. It took almost 20 minutes for the temperature to reach the new value after being set. The procedure was repeated at 1200^0C.

3.3.3.2 Slag – Metal Reaction Equilibria and Kinetics

The experimental procedure was the same as outlined above up to the stage of drawing out the sample at 1400^0C. After drawing the sample at 1400^0C, the slag was added to the mullite tube and held there for 30 minutes before taken out another sample. After cooling, one additional sample was taken from the solidified mass. Slag layer was duly removed from the sample by effecting hammering.

In another set of experiments, graphite crucible was used instead of the mullite tube In such cases samples were taken at regular interval of time to study the rate of extend of sulphur removal from the melt by the addition of slag.

3.4 Chemical Analysis of the samples

3.4.1 Sample Preparation

Samples were powdered to size less than 0.15 mm using a pestle and mortar. Non magnetic particles could be separated out using a bar magnet.

3.4.2 Manganese Analysis

0.1 gm of the powdered sample was dissolved in 20 ml of 1:3 nitric acid and boiled for 1- 2 minutes to expel oxide of nitrogen. The solution was then diluted to 60 ml, 5-10 ml of phosphoric acid and 0.5 gm of potassium iodate (KIO_3) were added. It was then boiled for 1 minute. The solution was cooled and made up to 100 ml in a volumetric flask. In case where manganese content was more then the instrumental analysis range, necessary dilution was made. The colour of the diluted solution was then matched against standard samples of known manganese content. The wave length of 530 μ was used in the calorimeter analysis. The apparatus was calibrated using standard steel samples and cast iron samples of known manganese content.

3.4.3 Carbon Analysis

Carbon analysis was done by using the strohlein apparatus. This is a very quick and efficient method for estimating carbon. The combustion furnace was heated to a temperature of 1150 – 1200^{0}C and the oxygen gas was passed through the

combustion tube into the absorption vessel which was filled with 30% KOH solution and it serves to absorb CO_2. The gas was collected until the measuring buret is almost filled and the cock was closed to prevent the entry of any further O_2. The measuring buret was connected with labeling bottle, which contains the sealing liquid. The level was adjusted in the normal way. The cock was then opened in such a way as to connect the absorption vessel with the measuring buret and the gas was passed twice in to absorption vessel. The remaining gas was again collected in the buret and the levels were again adjusted with the help of the leveling bottle. CO_2 was absorbed and the decrease in volume of the gas was recorded directly as percentage of carbon. A schematic diagram of strohlein apparatus is shown in *Fig-3.3.*

3.4.4 <u>Sulphur Analysis</u>

Procedure adopted for the analysis of sulphur in the present study is given below:

1. 5 gm of powder metal sample is taken in to conical flask.

2. 1 gm $CdCl_2$ was dissolved in a mixture of 36 ml of water and 24 ml concentrated ammonia in a conical flask.

3. 150 ml of preheated 1:1 HCl was poured drop by drop in the conical flask. The following reaction occurs:

$$[S] + HCl \rightarrow H_2S$$

Glass tube with stop cock

Carbon Buret
Absorption vessel

Furnace

Levelling Bottle

oxygen cylinder
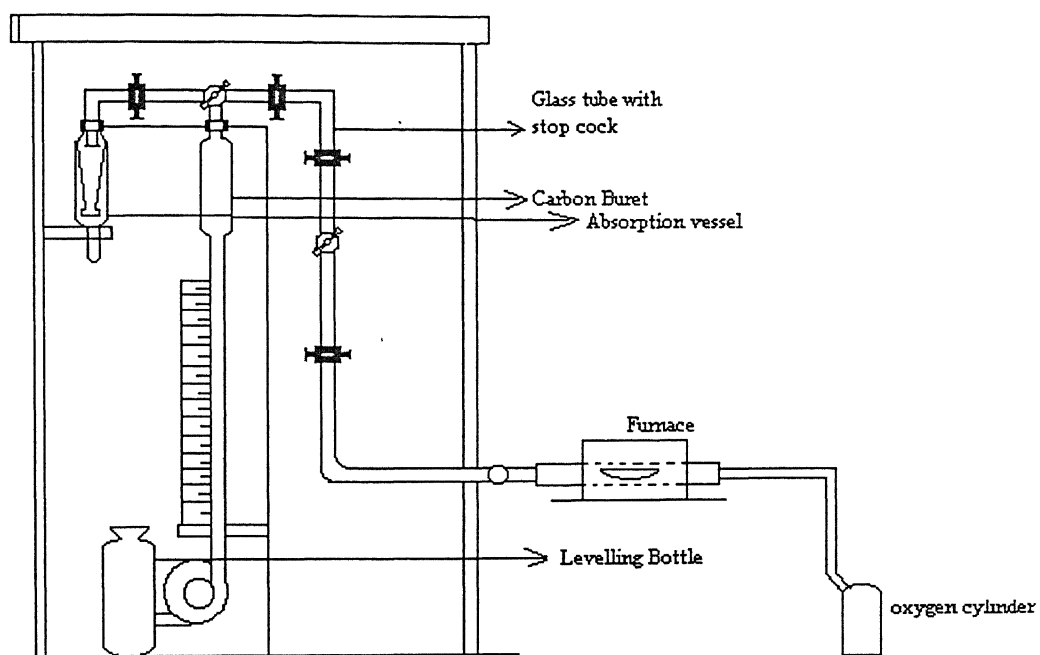
Fig 3.3: A Schematic Diagram of Strohlein Apparatus

4. H_2S is absorbed by the Ammonical $CdCl_2$ Solution to form yellow precipitate of cadmium sulphide.

5. Towards the end of the reaction heat supply is increased to produce steam and flush out the remaining H_2S.

6. The absorbing solution was acidified with 25 ml concentrated HCl and cooled in an ice bath.

7. 10 cc of N/10 iodine solution was added in the absorbing solution and titrated against N/40 $Na_2S_2O_3$ solution using starch as indicator.

8. The percent sulpher was given by

$$[\%S] = (12.4*64*100*y)/(w*500*248*N)$$

where y = amount of N/10 $Na_2S_2O_3$ consumed in milliliters,

w = weight of sample in grams, and

N = Normality of $Na_2S_2O_3$ solution.

CHAPTER IV
MODELS FOR SULPHUR DETERMINATION

4.1 Simplified Model

Presence of manganese in liquid iron carbon alloy would lower the solubility of sulphur due to formation of MnS as follows:

$$[\%Mn] + [\%S] = (MnS)$$
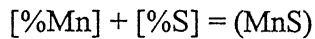
$$\ln(a_{MnS}/(f_S * f_{Mn} * [\%Mn]*[\%S])) = 18988.8/T - 11.569 \quad (1516 < T < 1803k) \qquad (4.1)$$

f_S & f_{Mn} are the activity coefficient of sulphur & manganese respectively with reference to the infinite dilute solution state on 1wt% standard state.

Turkdogan & Biswas have assumed f_{Mn} to be 0.8 for carbon saturated metal in the temperature range of 1400 to 1600^0C.

Activity of MnS (a_{Mns}) may be assumed to be unity for simplicity. For carbon saturated iron Turkdogan calculated f_S to be around 7 in the temperature range of $1300-1500^0C$ based on the thermodynamics of the reported data.

From above consideration, amount of sulphur at different manganese level and temperature may be calculated as follows:

$$[\%S] = 0.178/([\%Mn]*\exp(18988.8/T - 11.569)) \qquad (4.2)$$

At high levels of sulphur, presence of FeS in the slag may not be ignored. Slag – metal equilibrium will be represented by the equation (4.1) as well as by following reaction:

$$[\%Fe] + [\%S] = (FeS)$$
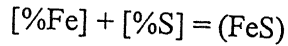
$$\ln (a_{FeS} / ([\%S]*f_S)) = -362.25/T - 1.5479 \qquad (4.3)$$

Activity of iron in the solution may be taken as unity. Assuming ideal solution, activity of MnS and FeS in the slag may be taken equal to its weight fraction as molecular weights of manganese and iron being 55 and 56 respectively are very close to each other, One may solve the following equations simultaneously:

$$\ln (X_{MnS} / ([\%Mn]*[\%S]*0.8*7)) = 18988.8/T - 11.569 \qquad (4.4)$$

$$\ln ((1-X_{MnS}) / ([\%S]*7)) = -362.25/T - 1.5479 \qquad (4.5)$$

Where X_{MnS} is weight fraction of MnS in the slag.

4.2 Development of a model to determine the composition of the melt due to addition of FeS and Mn to the carbon saturated melt of iron of known compositions.

Let X1 and X_2 be amounts of FeS and Mn added to 100 gm of carbon saturated iron of known composition. Melt composition can be determined by making material balance as well as considering the slag –metal equilibrium considerations.

Let Y and Z be amounts of melt and slag respectively after the addition then overall balance yields the following:

$$Y + Z = 100 + X_1 + X_2 \qquad (4.6)$$

Sulphur balance for the system gives the following equation:

$$([\%S]/100)*Y + 32/87*Z + 32*(1/88 - 1/87)*X_{FeS}*Z = (32/88)*X_1 + [\%S]_0 \qquad (4.7)$$

Manganese balance yields the following:

$$([\%Mn]/100)*Y + 55/87*(1-X_{FeS})*Z = X_2 + [\%Mn]_0 \qquad (4.8)$$

Where $[\%S]_0$, and $[\%Mn]$ are initial weight percent sulphur and manganese in the melt.

Manganese - Sulphur equilibrium may be represented by the followings:

$$([\%S]*[\%Mn]) / (1-X_{FeS}) = 1/ (f_S*f_{Mn}*\exp(18988.8/T- 11.569)) \qquad (4.9)$$

Iron – Sulphur equilibrium are as follows:

$$[\%S]/X_{FeS} = 1/ (f_S*\exp(-362.25/T – 1.5479)) \qquad (4.10)$$

There are five equations and five unknowns i.e. Y, Z, $[\%S]$, $[\%Mn]$, X_{FeS}. A computer program is used to solve these equations simultaneously.

Assumptions that are implied in the model above are summarized below:

(i) Activity co-efficients of sulphur and manganese are assumed to remain constant.

(ii) Change in the amount of carbon in the melt is ignored, due to change in composition of the melt.

(iii) Presence of silicon and phosphorus in the melt are ignored.

(iv) FeS and MnS in the slag form ideal liquid solution.

(v) Mole fraction of FeS in slag is same as its weight fraction.

(vi) Sulphur in the metal goes to the slag either as MnS or FeS.

(vii) There are no loss of any element due to vapourization.

Similarly model equations may be obtained when FeS and MnS are added to melt besides manganese metal.

4.3 **Results of Model Calculations**

Results of the computer calculations are reported below. Solutions of the model equations shows that sulpher contents of metal decreases with an increase in Mn content of alloy at a constant temperature or with a decrease in the temperature at constant Mn level of the bath. Activity of MnS is near unity in absence of any desulphuring agent. Activity of MnS would be lowered by adding certain fluxes as to produce liquid slag layer and sulphur should be reduced to a lower level.
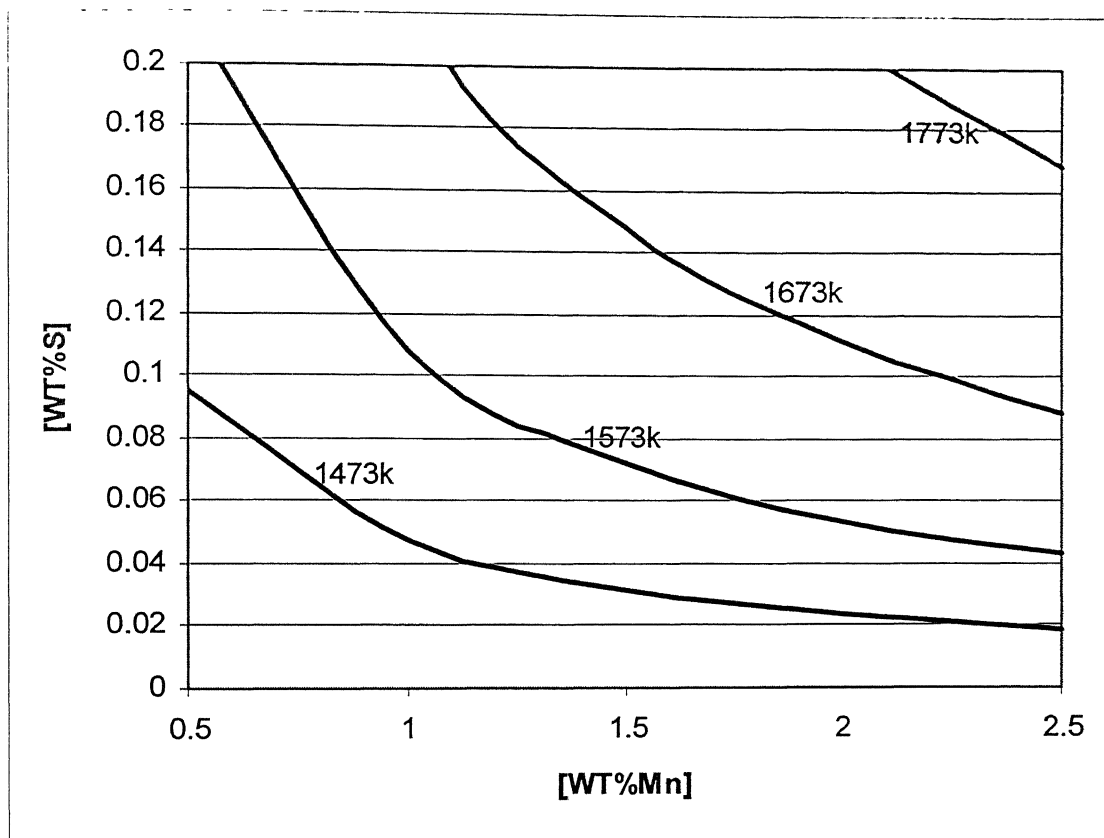
Fig 4.1: Plot of [WT%S] vs [WT%S] based on equation (4.3).

Fig 4.2: Plot of [WT%S] vs Temperature based on equation (4.3).

Effect of manganese on computed sulphur content of carbon saturated melt of iron.
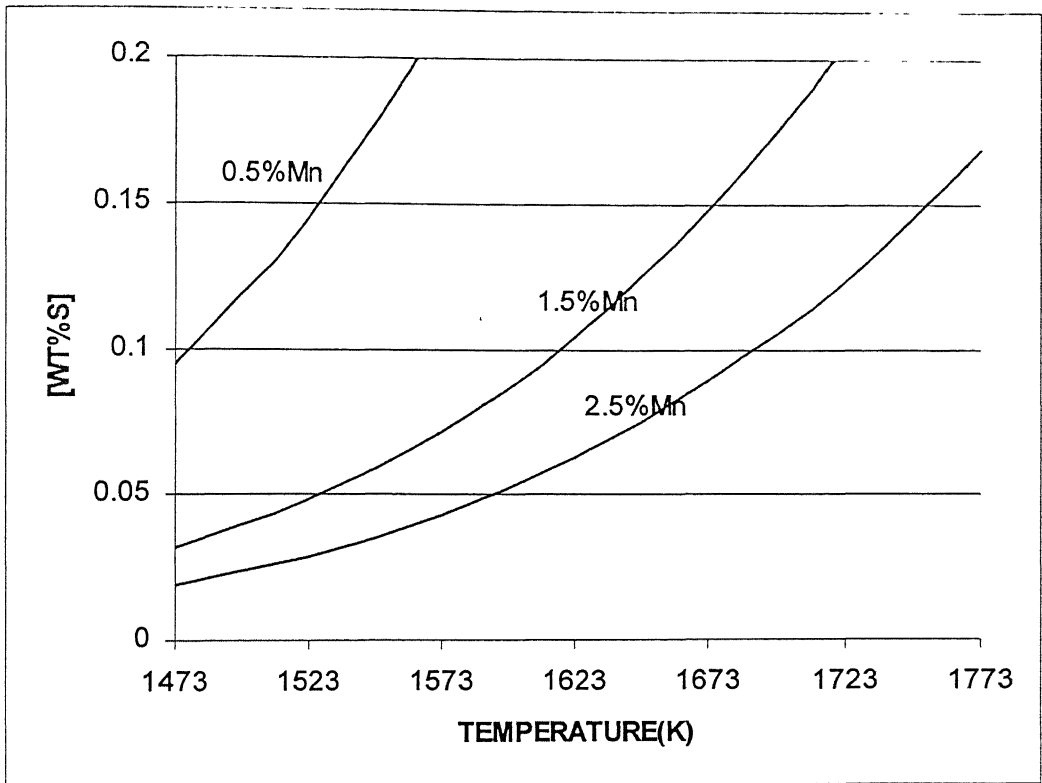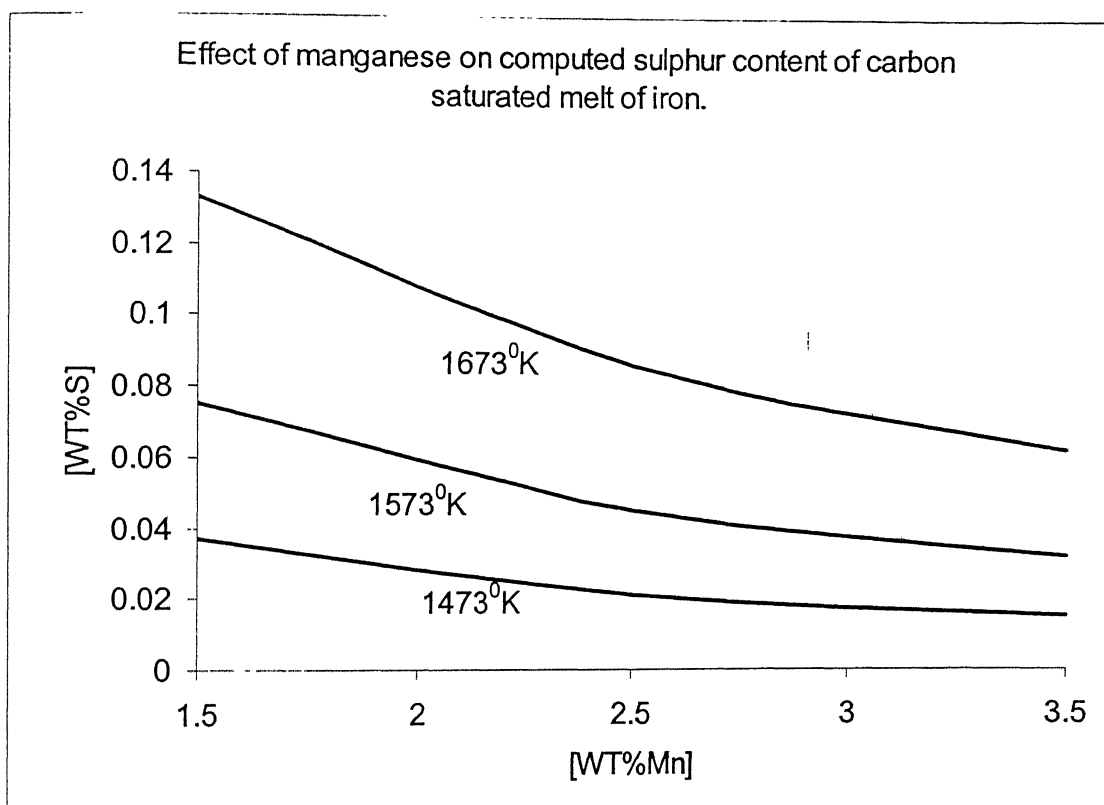
Fig 4.3: Plot of [WT%S] vs [WT%Mn] based on equation (4.4) and (4.5) and initial [WT%S] is equal to 0.2.
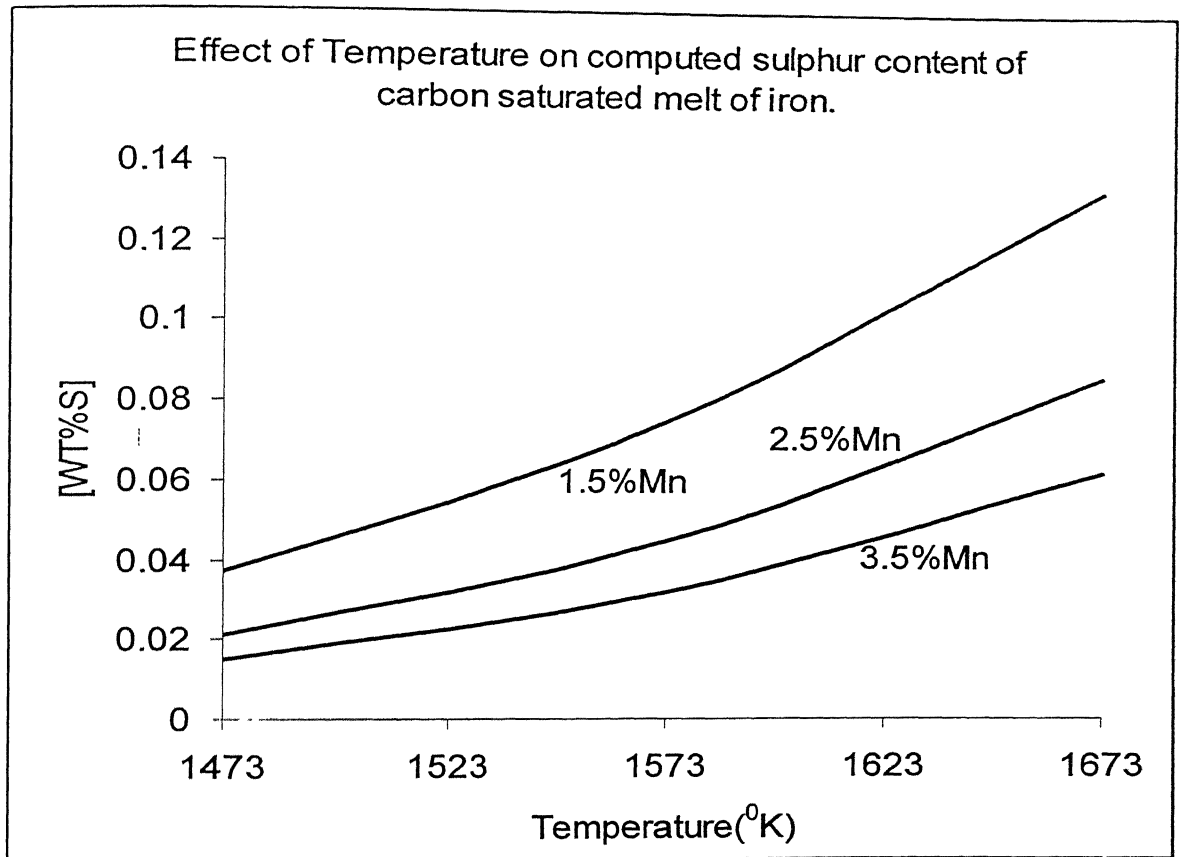
Fig 4.4: Plot of [WT%S] vs Temperature based on equation (4.4) and (4.5)

and initial [WT%S] is equal to 0.2.
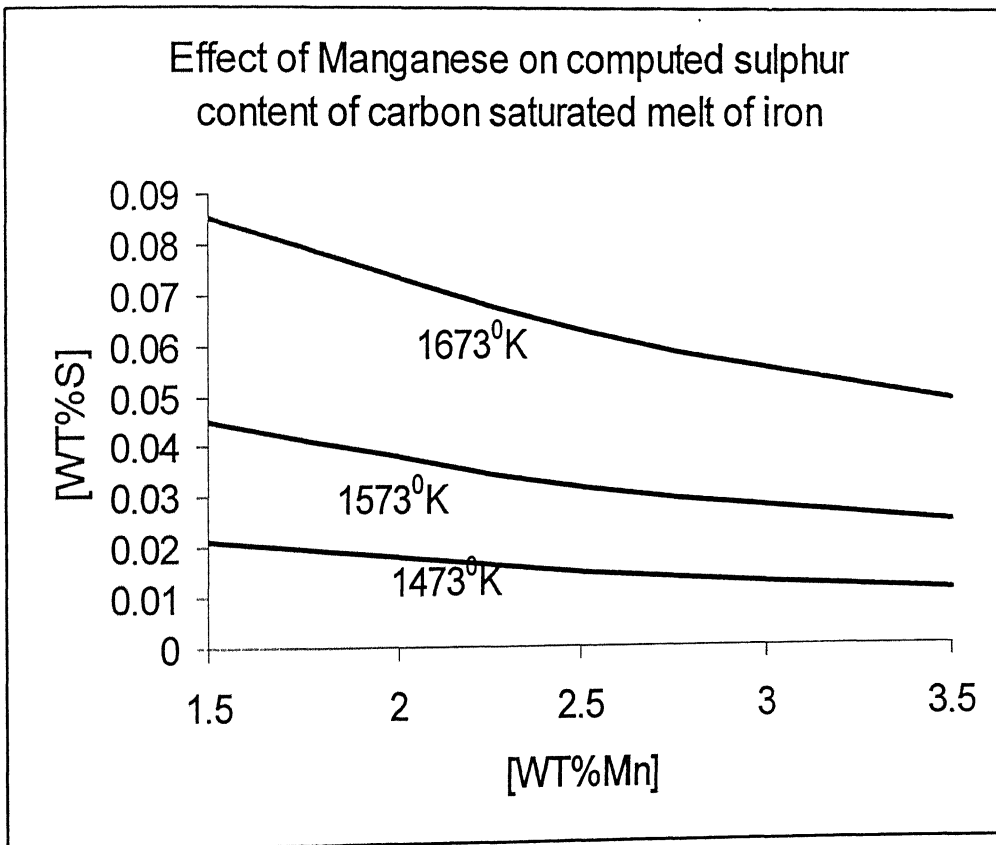
Fig 4.5: Plot of [WT%S] vs [WT%Mn] due to addition of 0.3 [WT%S] and 1.5 [WT%Mn] to the carbon saturated melt of iron of initial [WT%S] is equal to 0.2.

Effect of temperature on computed sulphur content of carbon saturated melt of iron.
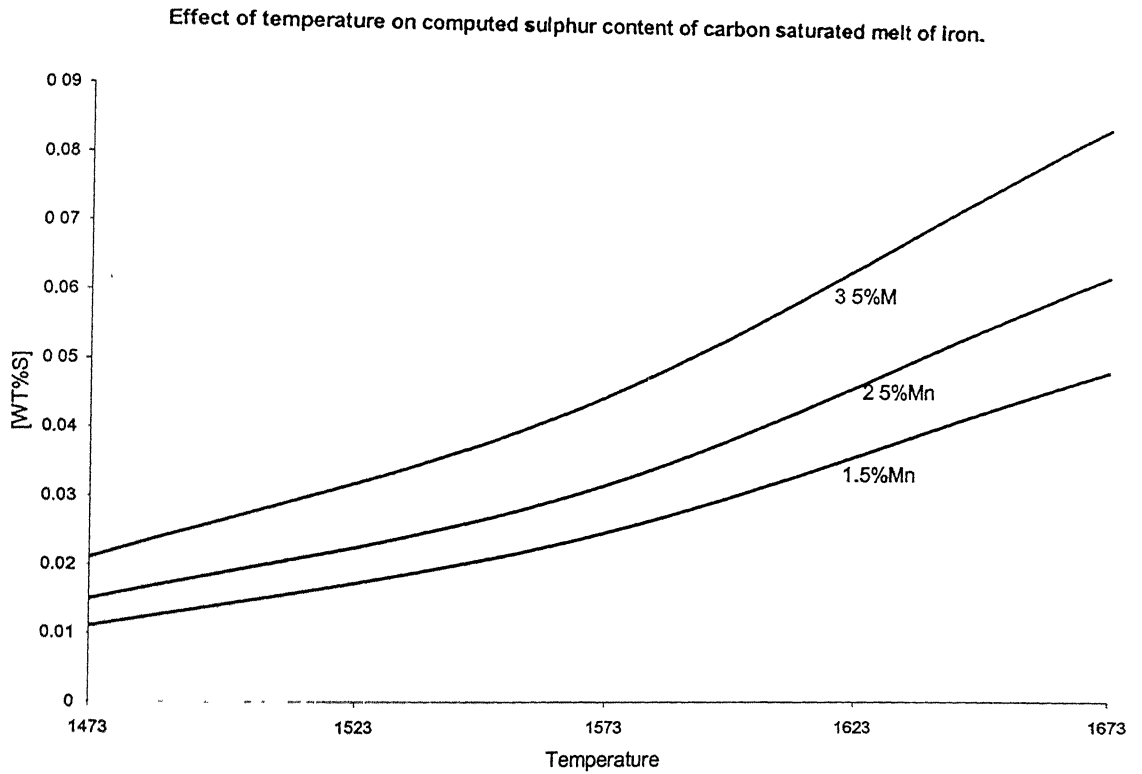
Fig 4.6: Plot of [WT%S] vs Temperature due to addition of 0.3 [WT%S] and 1.5 [WT%Mn] to the carbon saturated melt of iron of initial [WT%S] is equal to 0.2.

CHAPTER V

MODELLING OF THE LOWER PART OF THE BLAST FURNACE TO SEE THE EFFECT OF MANGANESE ORE ON COKE RATE AND IRON ORE.

5.1 Nomenclature

O_{en} : Oxygen enriched

x : moles H_2O / mole dry blast

f_{S_1} : weight fraction of Si in hot metal

f_{Mn} : weight fraction of Mn in hot metal

f_S : weight fraction of S in hot metal

f_C : weight fraction of C in hot metal

f_P : weight fraction of P in hot metal

T : hot metal temperature

T_{blast} : Blast temperature

T_{bosh} : bosh temperature

S_1 : %FeO in cast slag

g_1 : gangue to iron in iron ore

g_2 : gangue to (Mn + Fe) in Mn ore

b_1 : weight fraction of Fe in Fe ore

b_2 : weight fraction of Mn in Mn ore

b_3 : weight fraction of Fe in Mn ore

C_1 : weight fraction of ash in coke

C_2 : weight fraction of carbon in coke

C_3 : weight fraction of Fe_2O_3 in ash

R_{Mn} : Mn recovery

W_{HM} : Weight of Hot Metal

H_{CO} : Sensible heat of CO

H_{CO2} : Sensible heat of CO_2

H_{SiO2} : Sensible heat of SiO_2

H_{H2O} : Sensible heat of H_2O

H_{MnO} : Sensible heat of MnO

H_{P2O5} : Sensible heat of P_2O_5

H_{FeO} : Sensible heat of FeO

S_{HM} : Sensible heat of Hot Metal

S_{Slag} : Sensible heat of Slag

C_{PCO2} : Specific heat of CO_2

C_{PH2O} : Specific heat of H_2O

C_{PN2} : Specific heat of N_2

C_{PO2} : Specific heat of O_2

C_{PH2} : Specific heat of H_2

C_{PCO} : Specific heat of CO

$C_{Pgangue}$: Specific heat of gangue

C_{PCoke} : Specific heat of Coke

C_{PFeO} : Specific heat of FeO

Table 5.1 Operating and Thermal Data used in the Model Equations

Symbol	Value	Units
O_{cn}	2	%
x	0.05	Moles/mole
f_{Si}	0.01	
f_S	0.005	
f_P	0.002	
T	1773	^0K
T_{blast}	1173	^0K
T_{bosh}	1173	^0K
S_1	0.5	%
g_1	0.5	
g_2	0.5	
b_1	0.65	
b_2	0.45	
b_3	0.2	
C_1	0.187	
C_2	0.813	
C_3	0.1	
R_{Mn}	0.9	
W_{HM}	1000	Kg
H_{CO}	117697	J/mole
H_{CO2}	397002.5	J/mole
H_{SiO2}	949035	J/mole

Symbol	Value	Units
H_{H2O}	242760	J/mole
H_{MnO}	386400	J/mole
H_{P2O5}	1541400	J/mole
H_{FeO}	266700	J/mole
S_{HM}	1100	KJ/Kg
S_{Slag}	2000	KJ/Kg
C_{PCO2}	45	J/mole/^{0}K
C_{PH2O}	36	J/mole/^{0}K
C_{PN2}	31	J/mole/^{0}K
C_{PO2}	31	J/mole/^{0}K
C_{PH2}	31	J/mole/^{0}K
C_{PCO}	31	J/mole/^{0}K
$C_{Pgangue}$	1	J/mole/^{0}K
C_{PCoke}	1.5	J/mole/^{0}K
C_{PFeO}	54	J/mole/^{0}K

5.2 Introduction

Mathematical model equations are developed in this section to see the effect of manganese Ore on coke rate and iron ore content of the blast furnace. At lower part of the blast furnace, certain assumptions and simplifications of the process are made. The lower part is very critical for smooth running of the furnace from heat and chemical point of view. Mass and enthalpy balances are used to determine the required iron ore and coke rate at different manganese level of the hot metal. The lower part is separated from the upper part by a reserve zone where the temperature of gas is close to that of solid. Schematic to show the incoming and outgoing species in the lower part is shown in *Fig-5.1.* Besides direct and indirect reduction of $Fe_{0.95}O$ in the bosh and combustion reactions occurring in the raceway, other changes occurring in the lower part of the furnace may be described as below:

1. Carburizing of iron phase.

2. Melting of metal phase.

3. Melting of slag phase.

4. Reduction of oxides of nonferrous elements such as silicon, manganese and phosphorus etc.

5. Distribution of sulphur between slag and metal phases.

5.3 Assumptions

1. Hematite (Fe_2O_3) and magnetite (Fe_3O_4) are assumed to be pre reduced to wustite ($Fe_{0.95}O$) phase by carbon monoxide and hydrogen gases in the upper part.

2. There is gas solid equilibrium prevailing in the reserve zone as shown below:

$$Fe_{0.95}O + CO \ (g) = 0.95 \ Fe + CO_2 \ (g)$$

$$LogK_1 = 4300/4.606*T_{bosh} - 1.14 \qquad\qquad (4.11)$$

And $Fe_{0.95}O + H_2 \ (g) = 0.95 \ Fe + H_2O \ (g)$
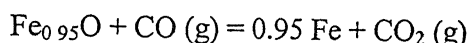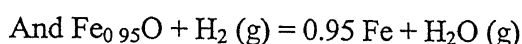
$$LogK_1 = 4300/4.606*T_{bosh} - 1.14 \qquad\qquad (4.12)$$

3. All P_2O_5 in burden is reduced in the bosh to give phosphorous in metal.

4. Recovery of manganese, R_{Mn} in hot metal is taken to be 90 pct. It may depend upon the slag composition.

5. Bosh and blast temperature are assumed to be 900^0C.

6. Heat loss in the lower part of the blast furnace is assumed to be 400 KJ per Kg of metal produced.

7. Sensible heats of slag and molten iron are assumed to be 2000 KJ/Kg and 1100 KJ/Kg respectively.
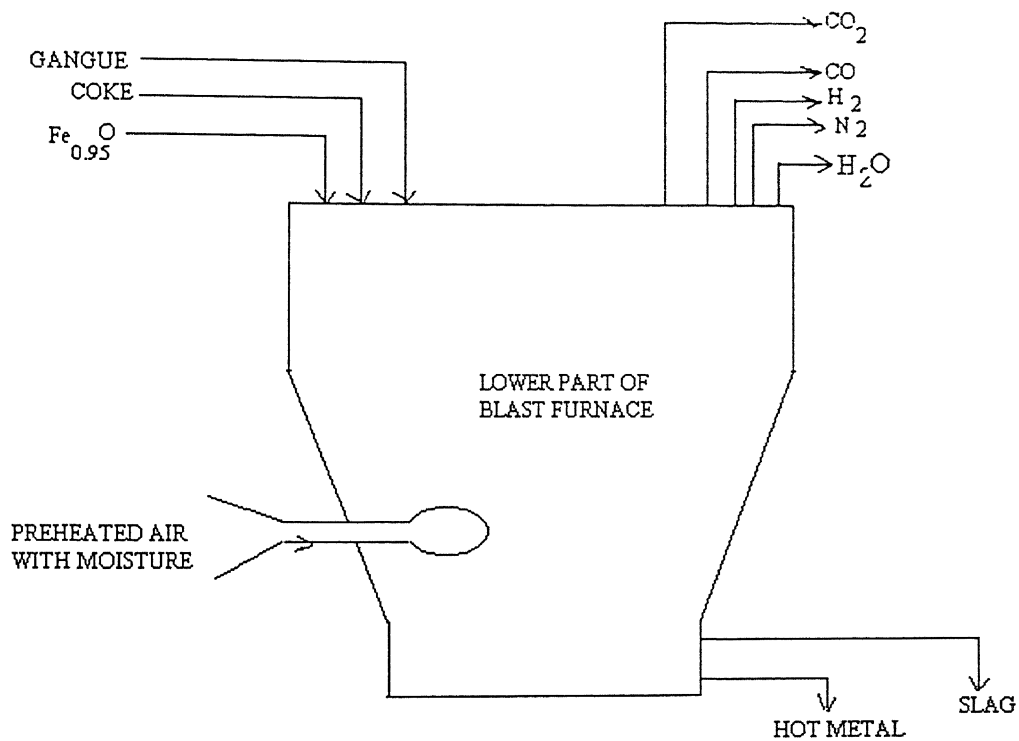
Fig 5.1: Schematic Material Flow in the Lower Part of the Furnace.

5.4 Model Equations

Model equations based on the heat and mass balance in the lower part of the furnace by taking 1000 kg of hot metal as the basis are summarized below. There are 12 linear equations with 12 unknown variables.

Oxygen balance for the system gives the following equation:

$$0.5*n_{CO} + n_{CO2} + 0.5*n_{H2O} - 0.5*n_{FeO} - (0.21 + O_{en} + x/2)*n_{blast}$$

$$= (f_{Si}/28 + f_{Mn}/110 + 2.5*f_P/62)*W_{HM} \qquad (4.13)$$

Iron balance may be represented by the followings:

$$0.95*56*n_{FeO} - S_1*0.95*56*W_{slag}/6900 = (1 - f_C - f_{Si} - f_{Mn} - f_P - f_S)*W_{HM} \qquad (4.14)$$

Where $100*f_C = 0.64 + 0.00254* T(K) + 3.4 * f_{Mn} - 34 (f_{Si} + f_P + f_S)$ $\qquad (4.15)$

Carbon balance yields the following:

$$Wc*C_2/12 - n_{CO} - n_{CO2} = (f_C / 12)* W_{HM} \qquad (4.16)$$

Nitrogen balance are as follows:

$$n_{N2} - n_{blast}*(1 - 0.21 - O_{en}) = 0 \qquad (4.17)$$

Hydrogen balance may be represented by the followings:

$$x*n_{blast} - n_{H2} - n_{H2O} = 0 \qquad (4.18)$$

Slag balance are as follows:

$$C_1*W_C + W_{gangue} - (1-S_1/100)*W_{slag}$$

$$= (f_{Si}*60/28 + (71*f_{Mn})/(55*R_{mn}) + 142*f_P/62 + f_S)*W_{HM} \quad (4.19)$$

Reduction of wustite may be represented by the followings:

$$n_{CO2} - K_1*n_{CO} = 0 \quad (4.20)$$

$$n_{H2O} - n_{H2}*K_2 = 0 \quad (4.21)$$

Gangue that enters the lower part of the furnace may be represented by the followings:

$$W_{gangue} - g_1b_1*W_{iore} - (g_2*(b_2+b_3) - 71*b_2/55)*W_{Mnore} = 0 \quad (4.22)$$

FeO balance is as follows:

$$0.95*56*n_{FeO} - b_1*W_{iore} - b_3*W_{Mnore} - C_1*C_3*W_C = 0 \quad (4.23)$$

Manganese balance yields the following:

$$b_2*W_{Mnore} = f_{Mn} * W_{HM}/R_{mn} \quad (4.24)$$

Heat balance gives the following equation:

$$((T_{blast}-298)*(C_{PO2}*(0.21+O_{en})+C_{PN2}*(1-0.21-O_{en})+CP_{H2O}*\lambda)) -x*H_{H2O})*n_{blast}$$

$$+ n_{FeO}*C_{PfeO}*(T_{bosh}-298) + (T_{bosh}-298)*C_{Pgangue}*W_{gangue}$$

$$+ (H_{CO}-C_{PCO}*(T_{bosh}-298.0))*n_{CO} + (H_{CO2}-CP_{CO2}*(T_{bosh}-298.0))*n_{CO2}$$

$$- C_{PH2}*(T_{bosh}-298.0)*n_{H2} +(H_{H2O}-CP_{H2O}*(T_{bosh}-298.0))*n_{H2O}$$

$$-C_{PN2}*(T_{bosh}-298.0)*n_{N2} + (-S_{SL}+(H_{FeO}*S_1*56*0.95/6900))*W_{slag}$$

$$+ (C_2*C_{Pcoke}+C_1*C_{Pash})*(T_{bosh}-298.0)*W_C$$

$$= (H_{SiO2}*f_{Si}/28.0+H_{MnO}*f_{Mn}/55.0+H_{P2O5}*f_P/62.0+S_{HM})*W_{HM}+H_{loss} \qquad (4.25)$$

Model Equations in the lower zone are solved simultaneously using the method of Gauss Elimination and computer programmed to obtain coke rate, slag rate, and to determine the required iron ore at different manganese level of the hot metal. **Table 5.1** shows the typical results of computation using model equations. Computed results are plotted in **Fig-5.2**. Details of the programme are given in the Appendix.

[%Mn] in Hot Metal	Slag rate (kg/ton)	Coke rate (kg/ton)	Iron ore (kg/ton)	Manganese ore (kg/ton)	[%C] in Hot Metal	[%Fe] in Hot Metal
0.0	538.2	511.2	1435.1	0.0	4.72	94.03
0.5	539.3	512.0	1423.4	12.3	4.74	93.51
1.0	540.3	512.9	1411.6	24.7	4.75	93
1.5	541.4	513.7	1399.8	37.0	4.77	92.48
2.0	542.5	514.6	1388.0	49.4	4.79	91.96

Table 5.2 Typical results of computation using model equations.
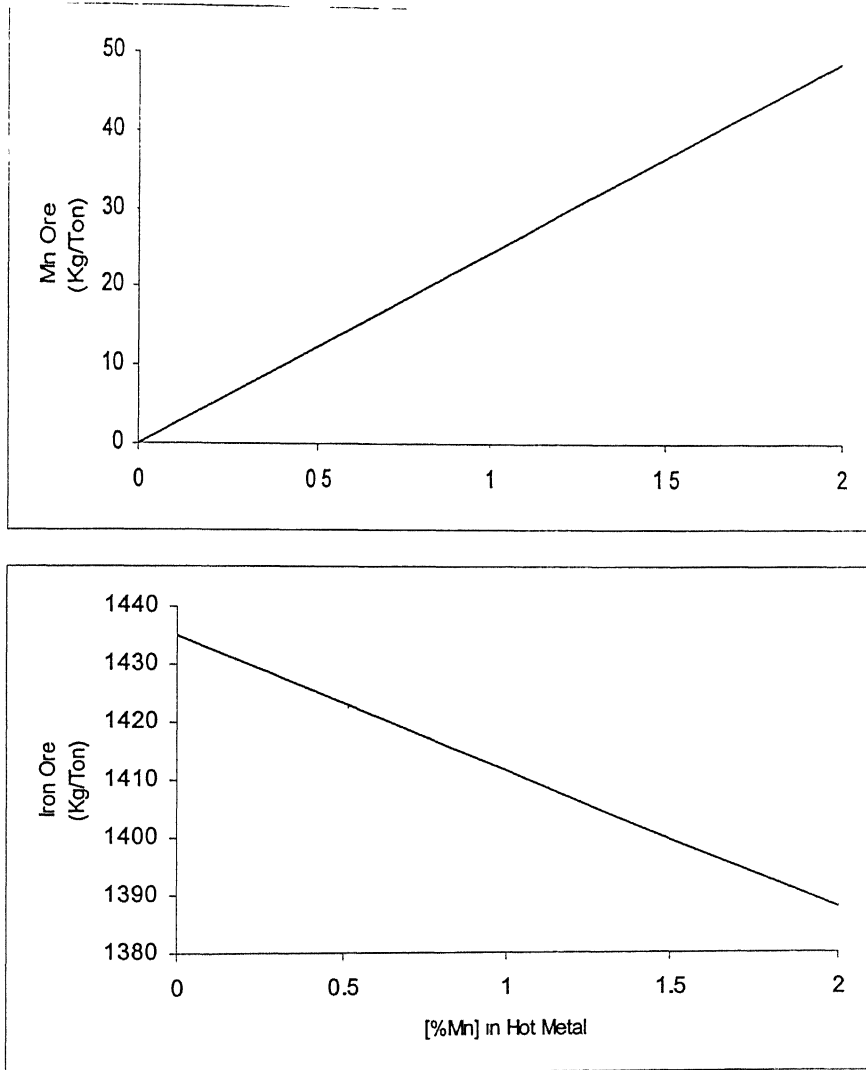
Fig 5.2 a: Required Fe and Mn – Ore vs Wt. % Mn in Hot Metal
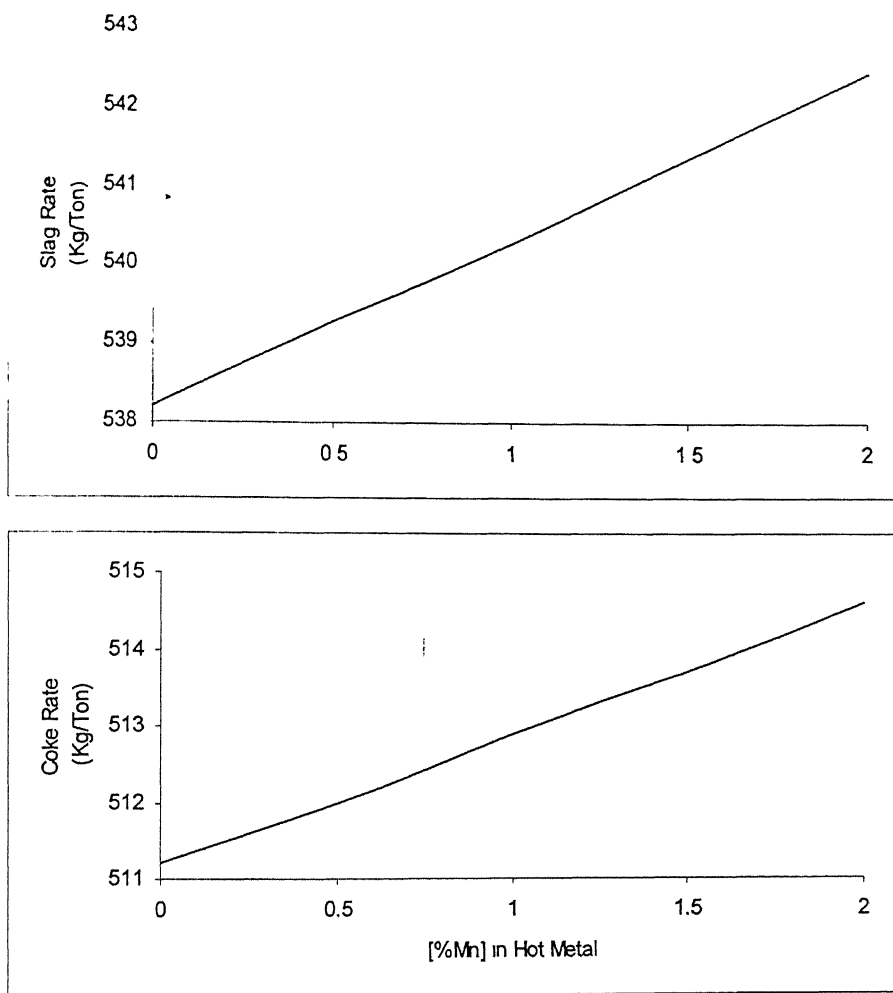
Fig 5.2 b: Coke rate, Slag Rate vs Wt. % Mn in Hot Metal

CHAPTER VI

RESULTS

Details of experiments carried out in the present study using the mullite tube and graphite crucible are included in *Table 6.1*. Experiments I, II, and III were done without the addition of slag to see the effect of manganese alone on sulphur content of bath at different temperature levels. As explained before samples were taken at three different temperatures. Experiments of remaining category were designed to see the effect by maintaining slag of different composition (basicity) on the sulphur content of metal at various manganese levels of the bath. In such experiments sample were taken from the melt at 1400^0C to determine sulphur content of metal before and after addition of slag. Experiments XIII and XIV were done with the graphite crucible. The solidified mass beneath the slag was also analysed for sulphur determination.

Results of sulphur determination in samples obtained from experiments I, II, and III are summarized in *Table 6.2*. Sulphur content of the standard samples was determined to ensure the reliability of the apparatus and the method used to analyze sulphur content of the metal. Determination of the sulphur content in the metal may be considered reliable because of the good agreement obtained between the experimentally determined values and the reported values for the standard samples as shown below:

Analysis No.	I	II	Avg.	Reported
[%S]	0.0544	0.0512	0.0528	0.057

Table 6.1: Details of Experiments carried out in the Present work.

Expt. No.	BF metal(g)	Fe / steel(g)	Carbon (g)	Manganese (g)	FeS (g)	Master slag (% of metal)	Basicity (CaO/SiO$_2$)
I	20	50	5	5.0	0.2	0.0	
II	20	50	5	2.5	0.2	0.0	
III	20	50	5	0.0	0.2	0.0	
IV	12.47	31.2	3.1	3.1	0.12	10	1.0
V	12.47	31.2	3.1	1.5	0.12	10	1.0
VI	12.47	31.2	3.1	0.0	0.12	10	1.0
VII	12.47	31.2	3.1	1.5	0.12	20	1.0
VIII	12.47	31.2	3.1	0.0	0.12	20	1.0
IX	12.47	31.2	3.1	1.5	0.12	10	0.8
X	12.47	31.2	3.1	0.0	0.12	10	0.8
XI	12.47	31.2	3.1	1.5	0.12	10	1.2
XII	12.47	31.2	3.1	0.0	0.12	10	1.2
XIII	12.47	31.2	3.1	1.5	0.12	10	0.8
XIV	12.47	31.2	3.1	0.0	0.12	10	0.8

Table 6.2. Result of Sulphur Determination in Metal Samples Collected with out the addition of slag.

Sl. No.	Sample	Expt. Temp.(^{0}C)	[Wt. % S]
1	I(a)	1400	0.0192
2	I(b)	1325	0.0170
3	I(c)	1250	0.0096
4	II(a)	1400	0.0416
5	II(b)	1325	0.0384
6	II(c)	1250	0.0352
7	III(a)	1400	0.099
8	III(b)	1325	-----
9	III(c)	1250	0.077

Results of sulphur determination in samples obtained from experiments due to addition of the slag of different basicity are summarized in *Table 6.3*. For all experiments it was ensured that there was no slag adhering to metal sample before doing any analysis. Solidified slag layer was removed by repeated hammering after breaking out the mullite tube.

Results of sulphur determination in samples obtained from experiments with graphite crucible due to addition of slag of basicity 0.8 are summarized in *Table 6.4*. From the table it is obvious that the sulphur level of metal decreases with time at constant Mn level of the bath.

Table 6.3: Results of Analysis of Metal Samples Collected in Experiments to Study Slag – Metal Equilibrium at 1400^0C.

Expt. No.	[Wt%S] Before addition of slag	[Wt%S] After addition of slag	[Wt%S] After cooling	Carbon analysis (%)	Manganese analysis (%)
IV	0 0192	0.0128	0 0096	2.89	2.16
V	0 032	0 0179	*	*	*
VI	0.0832	0 0352	0 0352	*	*
VII	0.0256	0 01432	*	3.45	1.72
VIII	0.08	0 0416	0.0416	*	*
IX	0.045	0.032	0.0224	*	*
X	*	0 0576	0.0288	1.84	0.7
XI	0 048	0 0384	0.0128	*	*
XII	0.0672	0 0512	*	*	*

* Not measured

Table 6.4: Result of Analysis of Metal Samples Collected in the experiments carried out in graphite crucible at 1400^0C.

Expt. No.	Time (mins) of taking the saples (after addition of slag)	[Wt. % S]	Carbon analysis (%)	Manganese analysis (%)
XIII	0	0.048	*	*
XIII	30	0.0352	3.09	2.02
XIII	60	0.0288	2.66	2.22
XIV	0	0.0864	*	*
XIV	30	0 0512	3.26	0.81
XIV	60	0.048	2.48	0.85

* Not measured

CHAPTER VII

DISCUSSION

Results of measured sulphur content of metal without any slag additions obtained in the present study are compared with the theoretical values using model equations in chapter IV as well as with those reported by other investigators in *Fig-7.1* and *Fig-7.2*. There is general agreement that as temperature decreases as constant manganese level or manganese content increases at constant temperature, solubility of sulphur in the melt decreases. The reaction between manganese and sulphur could occur through out the bulk of the melt and may lies to reach equilibrium in most of the cases. Manganese sulphide, thus formed could float to top due to its lower density.

Results in the present study show that by maintaining 10 wt% slag for 30 minutes above the melt, 20-35% drop in sulphur could occur. In some experiments, there was a significant drop in sulphur during solidifications. Results of sulphur determination before and after addition of slag and after solidification of metal are compared in *Fig-7.3*.

The slag – metal reaction can occur only at the slag metal interface. For effective removal of sulphur good degree of mixing of slag and metal phase is required. Measured sulphur content is plotted against time for two set of experiments in *Fig-7.4*.

In absence of stirring, slag metal reaction cannot account for the removal of sulphur from the melt in short period of treatment. On the other hand presence of manganese could remove sulphur from the bulk and its effect is more pronounced at lower
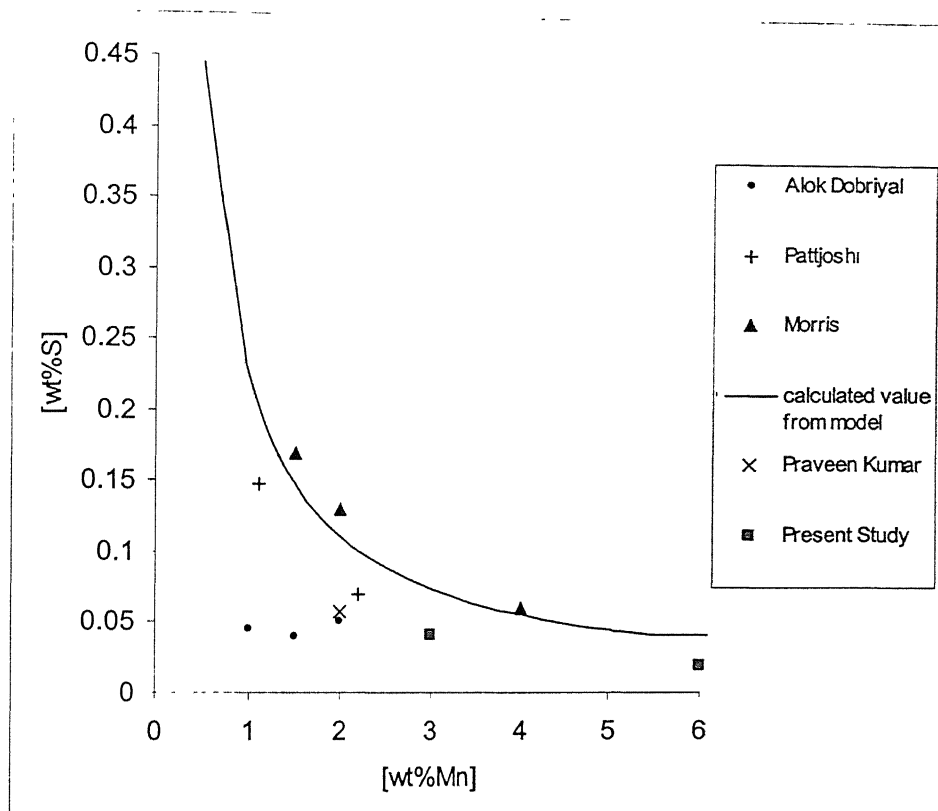
Fig-7.1: Effect of manganese on sulphur content of metal at 1400^{0}C.
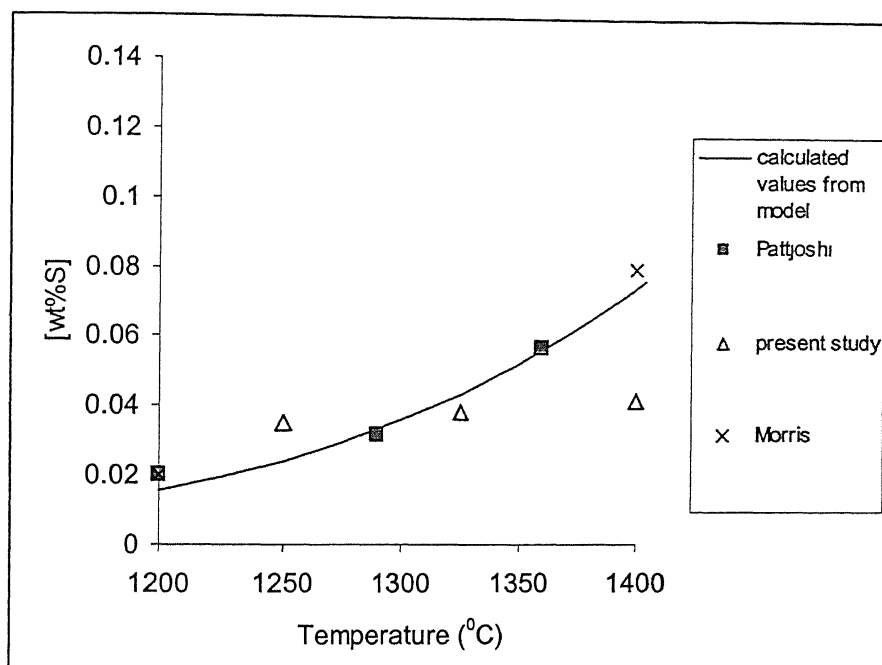
Fig-7.2: Effect of Temperature on sulphur content of metal at 3% manganese level in the melt.
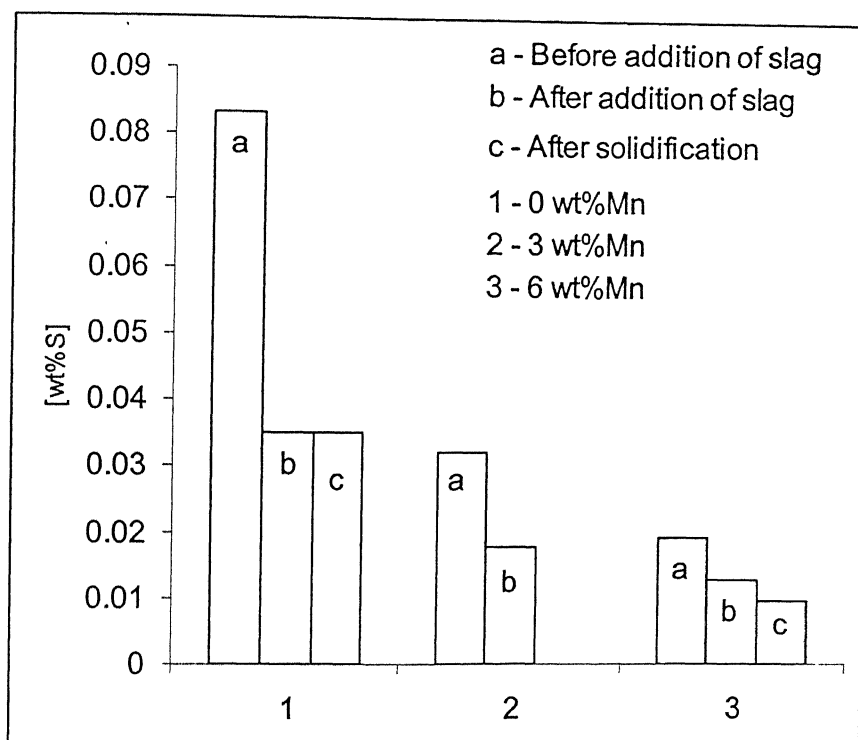
Fig 7.3 (a): Results of sulphur determination before and after addition of slag of basicity one and after solidification of metal with 10% slag volume.
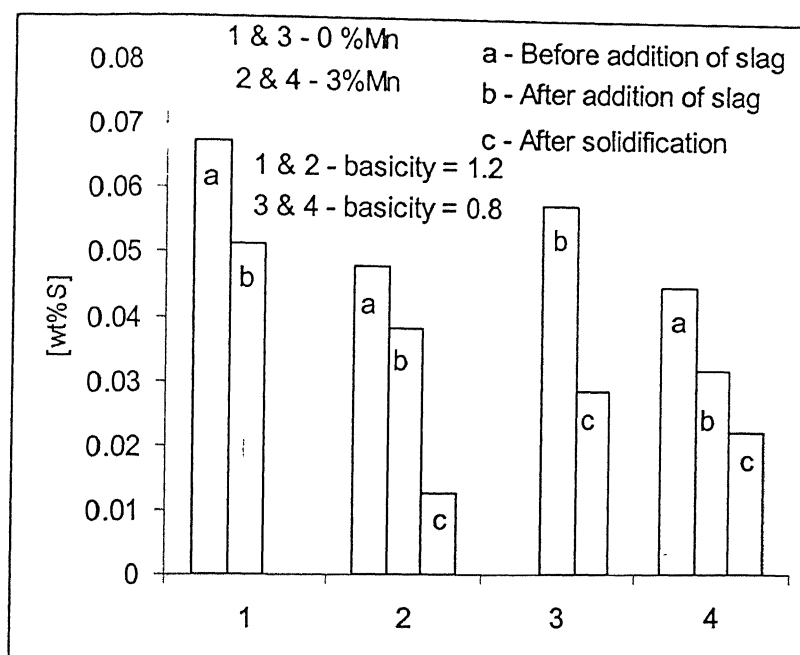
Fig 7.3 (b): Results of sulphur determination before and after addition of slags of basicity 1.2 and 0.8 and after solidification of metal with 10% slag volume.
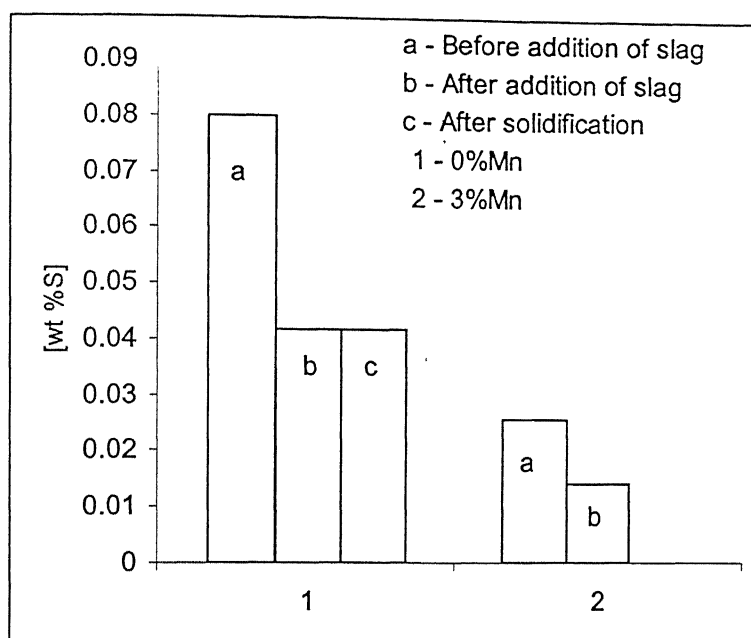
Fig 7.3 (c): Results of sulphur determination before and after addition of slag of basicity one and after solidification of metal with 20% slag volume.
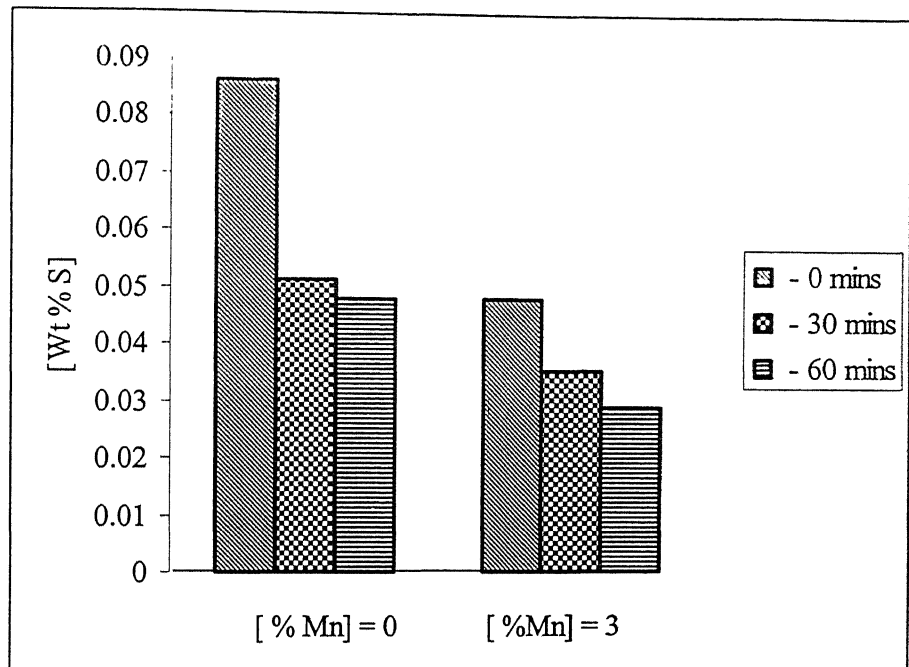
Fig-7.4: Measured sulphur content is plotted against time.

temperatures. Results of sulphur removal by the slag of different compositions obtained in the present study are compared with those obtained by Pattjoshi and Dobriyal in *Fig-7.5.*

There is wide scatter in the data due to sluggishness of the slag metal reaction as maintained before.

The advantage of removing sulphur to low values by maintaining 1to 2 pct manganese in metal may be weighed against the extra cost associated with manufactures of high manganese hot metal. Model results in chapter – V show that coke rate increases in a rate of 1.7 kg/ton for every 1 pct increase in manganese in hot metal. Also low cost iron ore must be replaced by more expensive manganese ore. Increase in cost of hot metal may be determined as follows:

$$\Delta C_{HM} = \Delta W_{coke} * C_{coke} + \Delta W_{Mnore} * C_{Mnore} - \Delta W_{Iore} * C_{Iore}$$

Where ΔC_{HM} = Increase in cost of hot metal

ΔW_{coke} = Increase in coke rate

C_{coke} = Cost of coke

ΔW_{Mnore} = Increase in manganese ore

C_{Mnore} = Cost of manganese ore

ΔW_{Iore} = Decrease in iron ore

C_{Iore} = cost of iron ore
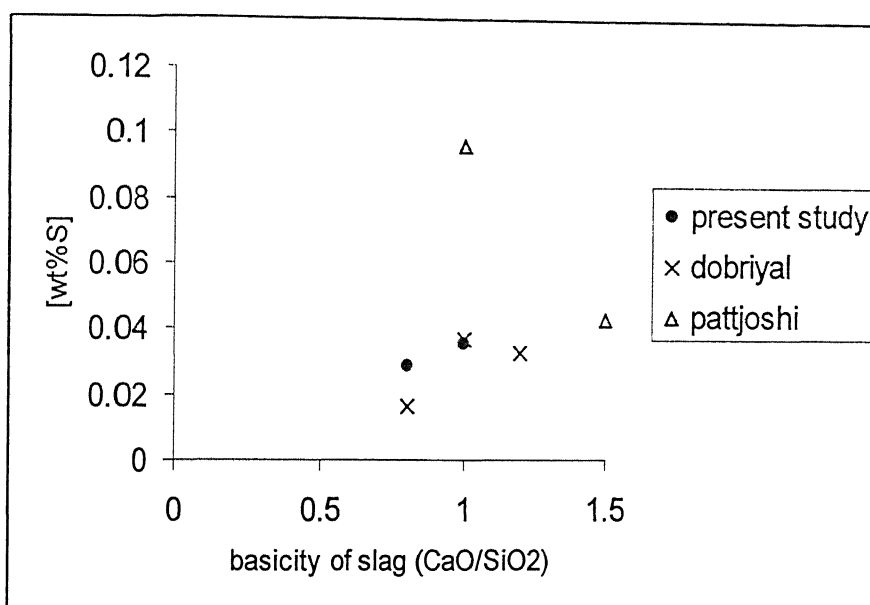
Fig- 7.5 Comparison of results obtained in the present study with those obtained by Pattjoshi[1] and Dobriyal[25].

The following facts must be kept in mind while deciding the operating parameters in the furnace.

(a) By having 1-2 % manganese in metal, sulphur may be removed to acceptable levels during transit of the hot metal from blast furnace to LD shop. Temperature of hot metal may decrease from 1400^0C to less than 1300^0C.

(b) The sulphur rich slag must be removed as completely as possible to avoid reversion of sulphur from slag to metal phase during oxygen steel making.

(c) Presence of manganese in metal may not require any external desulphurization of hot metal to control sulphur in steel.

(d) Presence of manganese in metal could result in thinning of the first slag formed during oxygen lancing due to early formation of MnO. This may prove to be advantageous in having smooth running of the converter without running problems of lance jam.

(e) As MnO is basic in nature, one may cut down the lime consumption in oxygen steel making to some extent.

(f) Iron metal yield will be lowered while refining metal with higher manganese content. Manganese recovery in metal may be as low as 30 pct.

(g) Oxygen requirement may also increase with an increase to manganese content of metal due to the oxidation of manganese.

Full discussion of the techno economics of producing hot metal with different manganese content is outside the scope of the present study.

CHAPTER VIII

SUMMARY AND CONCLUSION

1. Model equations based on materials balance and slag metal equilibrium have been developed and solved using a computer programme to determine sulphur content of the metal phase due to additions of different proportions of iron sulphide and manganese metal to blast furnace iron at different temperatures of the bath.

2. Results of model calculations show that sulphur content of metal decreases with an increase in manganese content of the bath at constant temperature. Results also reveal that sulphur content tends to fall with lowering of metal temperature at constant manganese content of the metal.

3. Model equations based on the heat and mass balance in the lower part of the blast furnace by taking 1000 kg of hot metal as the basis show that with 1% increase in manganese in hot metal coke rate increases in a rate of 1.7 kg / ton of hot metal.

4. One silicon carbide tube furnace has been designed and constructed in the laboratory to reach 1400^0C. Its temperature can be controlled within $\pm\ 5^0$C.

5. Samples of bath could be drawn at different temperatures during cooling stages. Reaction between manganese and sulphur occurred through out the bulk of the bath as to reach equilibrium levels.

6. Experiments were conducted to study the slag metal reaction at different manganese levels of the bath. The composition of slag was varied. Considerable stirring of the bath was needed to promote faster desulphurization of metal by the slag.

7. Practical importance of the study lies in the observed drop in sulphur content of hot metal in the ladle during its transport from the blast furnace to mixer stage in the steel making shop whenever the manganese content of metal exceeded one percent. Further drop in sulphur may be envisaged if slag is added to decrease the activity of manganese sulphide but this may require extensive stirring of the bath.

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APPENDIX

1. Computer Programme to Solve Model Equations in Lower Part of Blast Furnace.

```c
#include<stdio.h>
#include<math.h>

#define nr 12
#define nc 12

main()
{
int i,j,k,lin_ind,I[nc];

int t=1773,tb=1173,tbo=1173,Whm=1000,Hloss;

float Oen=0.02,x1=0.05,fsi=0.01,fmn=0.0,fp=0.002,fs=0.0005,fc,s1=0.5,g1=0.5,g2=0.5,
c1=0.187,c2=0.813,c3=0.1,b1=0.65,b2=0.45,b3=0.2,R1=0.9,k1,k2,Pc,Pfe,Pmn;
float Hco=117697,Hco2=397002.5,Hh2o=242760,Hsio2=949035,Hmno=386400,
Hfeo=266700,Hp2o5=1541400,Ssl=2000,Shm=1100;
float Cpco=31,Cpco2=45,Cph2=31,Cph2o=36,Cpn2=31,Cpgangue=1,Cpash=1,Cpc=1.5,
Cpfeo=54,Cpo2=31;
float a[nr][nc],b[nr],x[nc],tmp1,tmp2, tmpp,y,factor;
FILE *fpa;
fpa=fopen("model3.txt","w");

fprintf(fpa,"...............RESULTS OF MODEL EQUATIONS.....................");
fprintf(fpa,"\n\n\n\n");

fprintf(fpa,"Manganese Slagrate  Cokerate   Mnore   Ironore   Carbon Iron ");

fprintf(fpa,"\n\n\n");

fprintf(fpa," (%)      (Kg/ton)  (Kg/ton)    (Kg)     (Kg)      (%)  (%) ");
fprintf(fpa,"\n\n");

for(fmn=0.0;fmn<=0.02;fmn+=0.005)
        {
for(i=0;i<nc;i++)
        I[i] = i;

for(i=0;i<nr;i++)
        {
        for(j=0;j<nc;j++)
        a[i][j]=0.0;
```

```
        b[i]=0.0;
        }
Hloss=400*Whm;
fc=(0.64+0.00254*t+3.4*fmn-34*(fsi+fp+fs))/100;
Pc=100*fc;
Pfe=100*(1.0-fc-fsi-fmn-fp-fs);
k1=exp(2.303*((4300/(4.606*tbo))-1.14));
k2=exp(2.303*((-4350/(4.606*tbo))+0.51));
//fprintf(fpa,"%4.2f,%4.2f,%f",k1,k2,fc);



/* Row: 0-oxygen balance; 1-iron balance; 2-carbon balance;
   3-nitrogen balance; 4-hydrogen balance; 5-gangue balance;
   6-FeO+CO=Fe+CO2; 7-FeO+H2=Fe+H2O; 8-gangue balance;
   9-FeO balance; 10-Mn balance; 11- heat balance

  Col: 0-nblast; 1-nFeO; 2-Wgangue; 3-nCO; 4-nCO2; 5-nH2; 6-nH2O;
     7-nN2; 8-Wslag; 9-Wc; 10-Wiore; 11-Wmnore     */

a[0][0]=-(0.21+Oen+x1/2);
a[0][1]=-0.5;
a[0][3]=0.5;
a[0][4]=1.0;
a[0][6]=0.5;

a[1][1]=56*0.95;
a[1][8]=-(s1*0.95*56/6900);

a[2][3]=-1.0;
a[2][4]=-1.0;
a[2][9]=(c2/12.0);

a[3][0]=-(1.0-0.21-Oen);
a[3][7]=1.0;

a[4][0]=x1;
a[4][5]=-1.0;
a[4][6]=-1.0;

a[5][2]=1.0;
a[5][8]=-(1.0-s1/100);
a[5][9]=c1;

a[6][3]=-k1;
a[6][4]=1.0;
```

```
a[7][5]=-k2;
a[7][6]=1.0;

a[8][2]=1.0;
a[8][10]=-g1*b1;
a[8][11]=-g2*(b2+b3)-71*b2/55;

a[9][1]=56*0.95;
a[9][9]=-c1*c3;
a[9][10]=-b1;
a[9][11]=-b3;

a[10][11]=b2;

a[11][0]=(((tb-298.0)*(Cpo2*(0.21+Oen)+Cpn2*(1-0.21-Oen)+Cph2o*x1))-x1*Hh2o);
a[11][1]=Cpfeo*(tbo-298.0)-Hfeo;
a[11][2]=(tbo-298.0)*Cpgangue;
a[11][3]=(Hco-Cpco*(tbo-298.0));
a[11][4]=(Hco2-Cpco2*(tbo-298.0));
a[11][5]=-Cph2*(tbo-298.0);
a[11][6]=(Hh2o-Cph2o*(tbo-298.0));
a[11][7]=-Cpn2*(tbo-298.0);
a[11][8]=-Ssl+(Hfeo*s1*56*0.95/6900);
a[11][9]=(c2*Cpc+c1*Cpash)*(tbo-298.0);


b[0]=Whm*(fsi/28.0+fmn/110.0+2.5*fp/62.0);
b[1]=Whm*(1.0-fc-fsi-fmn-fp-fs);
b[2]=fc*Whm/12.0;
b[5]=(60*fsi/28.0+71.0*fmn/55.0+142.0*fp/62.0+fs)*Whm;
b[10]=fmn*Whm/R1;
b[11]=(Hsio2*fsi/28.0+Hmno*fmn/55.0+Hp2o5*fp/62.0+Shm)*Whm+Hloss;


for(i=0;i<nr;i++)
        {
                for(j=i+1;j<nr;j++)
                {
                        lin_ind=0;
                        factor = ((a[i][0]*1000000)/a[j][0]);
                        for(k=0;k<nc;k++)
                                if((a[i][k]*1000000)!=factor*a[j][k])
                                        lin_ind=1;
                        if(lin_ind==0)
                        {
                                if((b[i]*1000000)==(factor*b[j]))
```

```
                                    {
                                            fprintf(fpa,"\nINFINITE SOLUN\n");
                                            return,
                                    }
                                    else
                                    {

                                            fprintf(fpa,"\nNO SOLUN\n");
                                            return;
                                    }
                            }
                            /* else do nothing */
                    }
            }

    for(j=0;j<nc-1;j++)
        {
        if(a[j][j]==0)
        {
                for(i=j+1;i<nc;i++)
                        if(a[j][i]!=0)
                                break;
                /* now interchange col[i] with col[j] */
                for(k=0;k<nr;k++)
                {
                        tmp1 = a[k][i];
                        a[k][i] = a[k][j];
                        a[k][j] = tmp1;
                }
                        tmp2 = I[i];
                        I[i] = I[j];
                        I[j] = tmp2;

        }
        for(i=j+1;i<nr;i++)
        {
                tmpp = a[i][j];
                for(k=0;k<nc;k++)
                        {

                        a[i][k]=a[i][k]-a[j][k]*(tmpp/a[j][j]);
                }
        b[i]=b[i]-b[j]*(tmpp/a[j][j]);

        }
}
```

//finding out the values of the variables............

```
x[nr-1]=b[nr-1]/a[nr-1][nc-1];
for(i=nr-2;i>=0;i--)
                {
                y=b[i];
                for(j=nc-1;j>i;j--)
                        {
                        y=y-x[j]*a[i][j];
                        }
                x[i]=y/a[i][i];

                }


//displaying the values of the variables
Pmn=fmn*100;
fprintf(fpa,"\n \n");
fprintf(fpa," %4.1f ",Pmn);
for (i=8;i<=nr-1;i++)
        {

                fprintf(fpa,"%8.1f   ",x[i]);

        }
fprintf(fpa,"%   4.1f  %4.1f\n ",Pc,Pfe);


}
}
```

............RESULTS OF MODEL EQUATIONS.....................

Manganese	Slagrate	Cokerate	Mnore	Ironore	Carbon	Iron
(%)	(Kg/ton)	(Kg/ton)	(Kg)	(Kg)	(%)	(%)
0.0	538.2	511.2	0.0	1435.1	4.7	94.0
0.5	539.3	512.0	12.3	1423.4	4.7	93.5
1.0	540.3	512.9	24.7	1411.6	4.8	93.0
1.5	541.4	513.7	37.0	1399.8	4.8	92.5
2.0	542.5	514.6	49.4	1388.0	4.8	92.0